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SYNTHESIZED POLYIMIDE MEMBRANES FOR PERVAPORATION SEPARATIONS OF TOLUENE/ISO-OCTANE MIXTURES

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SYNTHESIZED POLYIMIDE MEMBRANES FOR PERVAPORATION SEPARATIONS OF TOLUENE/ISO-OCTANE MIXTURES

by

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To

My parents

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SYNTHESIZED POLYIMIDE MEMBRANES FOR PERVAPORATION SEPARATIONS OF TOLUENE/ISO-OCTANE MIXTURES

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Separation of aromatic/aliphatic hydrocarbon mixtures by pervaporation has been of increasing interest in recent decades. Dozens of polymer materials have been reported for separations of benzene/cyclohexane and toluene/iso-ocatne mixtures. However, fundamental understanding of material structure and transport relations is not adequate to generalize guidelines for materials screening. The goals of this study are to tailor the structure of the polyimide materials, correlate the structure and transport relations, and establish guidelines for future materials.

The 3, 5-Diaminobenzoic acid (DABA) containing polyimides were synthesized by both chemical and thermal solution imidization. The synthesized polyimides were formed into

dense films by solution casting. The physical properties of the polyimides synthesized with monomers**:** 2, 2-bis (3, 4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), 4, 6-trimethyl-1, 3-phenylendiamine (DAM) and DABA, were characterized by DSC, WAXD, GPC and density. The chemical structures were assessed by FTIR and NMR. The pervaporation and sorption of the synthesized polyimide membranes were tested in toluene/iso-octane mixtures at 100°C. The structure- transport property relations were established for the 6FDA-DAM/DABA membranes. The 6FDA-DAM/DABA polyimides were crosslinked by ethylene glycol. The pervaporation and sorption of the crosslinked membranes were tested in toluene/iso-octane mixtures at 100°C.

Thermal imidization was found to give a higher imidization degree than chemical imidization. As a result, the polyimides made by chemical imidization contain a higher percentage of carboxylic acid groups than those made by thermal imidization. Chemical imidization gives higher film density, glass transition temperature and lower flux and higher selectivity for the toluene/iso-octane pervaporation than the thermally imidized membranes because of the higher carboxylic acid concentration.

The chemically imidized membranes are slightly brittle after the crosslinking. Only the thermal imidization membranes have good flexibility and its pervaporation selectivity improves significantly after the crosslinking.

Solubility selectivity and diffusivity selectivity of the 6FDA-DAM/DABA membranes were correlated with solubility parameters and fractional free volume, respectively. The structure-mass transport relations show that for the 6FDA-DAM/DABA membranes, both solubility selectivity and diffusivity selectivity contribute to the pervaporation selectivity. For the chemically imidized membranes, increased DABA concentration has a positive effect on solubility selectivity and diffusivity selectivity. For the thermally imidized membranes, increased DABA concentration has a significant effect on diffusivity selectivity only.

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Chapter 1 Introduction

Aromatic and aliphatic hydrocarbons, such as benzene, toluene, hexane, etc., are widely used in industry as raw chemical materials and solvents. In 2002 the global capacity of benzene and toluene was 43 million and 20 million tons, respectively, representing a multi-billion dollar market. All gasoline available in the market contains some amount of aromatics. EPA has regulated a reduction of benzene concentration in gasoline from 5% to 1% by 2008. Considering the 137 billion gallons of gasoline US consumed in 2003, the potential of aromatic/aliphatic hydrocarbon mixtures separations is huge. However, the processes for separations of aromatics from the aliphatic components are among the most challenging in the petrochemical industry, since these components often have close boiling points or azeotropes. The currently used separation processes, such as extractive distillation, are complex in nature and/or involve high energy consumption, so there is a significant incentive to explore new process options for these separations.

1.1 Pervaporation for aromatic/aliphatic separation

Pervaporation (PV) is a promising alternative to current commercial processes due to its simplicity and potential for energy savings. Unlike distillation, the separation mechanism in pervaporation is not limited by the relative volatility of the components but relies mainly on the difference in sorption and diffusion properties of the feed components in the membrane. Thus, the nature of the membrane selected can be a useful tool for tuning the separation. However, industrial scale applications of pervaporation, particularly for

hydrophobic mixtures, have been limited in part by inadequate membrane performance and high membrane cost. Good membrane performance requires high selectivity and acceptable permeability, which involves some trade-off to optimize these properties in practical PV processes for aromatic/aliphatic separations. However, permeability can be compensated by reducing membrane thickness (e.g., composite membranes). Thus, economical polymeric membrane material development is a key issue for eventual implementation of this technology.

1.1.1 Polymer materials for the pervaporation

Refinery streams contain a wide spectrum of component molecules whose content and identity vary enormously according to the source of feedstock and process situations. It is not feasible to address the full spectrum of binary or multi-component combinations of aromatic/aliphatic compounds in a research program whose primary objective is to identify materials or materials concepts that may be broadly useful in this general type of application. Therefore, in this study, as in our prior work [1, 2], we have selected toluene and iso-octane as somewhat representative of components from a heavy cat naphtha in which the petrochemical industry has expressed interest. Polymeric materials reported in the literature that show promising performance for the separation of toluene/iso-octane mixtures by pervaporation can be classified into two groups. One group includes copolymers with soft segments providing high affinity for toluene and hard segments that provide structural integrity and limit swelling [3-7]. Such materials may be based on polyimides, polyesters, polyurethanes etc. The second group operates primarily by size

and shape mobility selectivity and includes polymers modified by crosslinking including covalent, ionic or charge transfer crosslinks, or plasma-graft filling [8-11].

1.1.2 Polyimide materials for pervaporation

Polyimides have proved to be attractive membrane materials in both of the above general groupings of materials. In fact, polyimides are good candidates for separations of gas, vapor and liquid mixtures due to their excellent thermal stability, chemical resistance, and rigidity of the chain backbone. Tanihara et al have examined polyimide materials prepared from 3,3', 4,4'-biphyenyl tetracarboxyphenyl dianhydride (BP) and methyl-substituted phenylenediamines for the separation of benzene /cyclohexane mixtures by pervaporation [1, 2]. These polyimides displayed high permeability but low selectivity and poor membrane durability due to high membrane swelling. Introduction of 3, 5-diaminobenzoic acid (DABA) into the polyimides led to membranes that showed higher performance and excellent durability because of the reduced membrane swelling [10]. The gas permeation characteristics of polyimide materials based on 2, 2-bis (3, 4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) or 4, 6-trimethyl-1, 3-phenylendiamine (DAM) have been extensively studied [13, 14]. Addition of the fluoro and methyl substituents increases the solubility of these polyimides. It is possible to use common solvents for film casting or composite membrane processing.

It was of interest to investigate these materials for pervaporation, but their significant swelling tendency in organic solvents required a strategy to optimize this property. 3, 5-

Diaminobenzoic acid (DABA) can facilitate packing, add polarity, and lend crosslinking sites via the carboxylic acid group, thereby providing a tool for structure-permeability optimization.

1.2 Overview of the dissertation

This dissertation reports on 6FDA-DAM/DABA based polyimide materials that were synthesized for the PV separation of toluene/iso-octane mixtures. The structure-tightening characteristics of the polar DABA monomer are examined in detail as part of developing a broader understanding of the structure-transport relations are initiated. The effect of different imidization methods in the properties of polyimide membranes is investigated and the crosslinking characteristics are discussed.

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Chapter 2 Brief literature summary of polyimide synthesis and film preparation

2.1 Two-step synthesis

A two-step method is the most commonly used procedure for polyimide synthesis. It includes reacting dianhydrides and diamines at ambient temperature in a dipolar aprotic solvent such as, N-methylpyrrolidinone (NMP) or N, N-dimethylacetamide (DMAc) to yield the corresponding polyamic acid, which is then cyclized into the polyimide.

2.1.1 Formation of polyamic acid

Addition of dianhydrides to diamines in a polar aprotic solvent at ambient temperature leads to the formation of the polyamic acid due to the necleophilic attack of the amino group on the carbonyl carbon of the dianhydride groups. Figure 2.1 shows the reversible reaction leading to the opening of the anhydride ring to form an amic acid group [1]. The forward rate constant for the reaction is generally several orders of magnitude larger than that of the reverse reaction and, thus, the reaction often appears irreversible if pure reagents are utilized [2]. For the reverse reaction to take place, the carboxyl proton needs to attack the adjacent polyamic acid groups [3]. Thus, any reagent that hinders this reaction can decrease the rate of the reverse reaction and, thus, can shift the equilibrium forward.

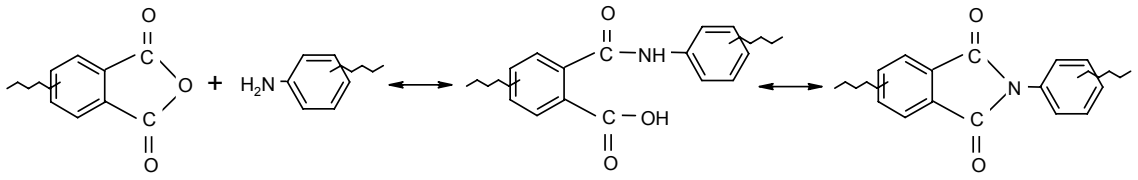

Figure2.1. Generalized reaction mechanism of aromatic imide formation

Polar aprotic solvents form strongly hydrogen bonded complexes with the free carboxyl groups and lead to an equilibrium constant in excess of 105 l/mol at ambient conditions [2]. However, if the reaction is in ether or hydrocarbon solvents, differences in equilibrium constant are observed depending upon the amine's basicity and the dianhydride's electrophilicity [4]. It is also important that the polyamic acid formation is exothermic and the equilibrium is favored at lower temperatures [5]. However, the equilibrium is shifted so far to the right at ambient temperature that further lowering of the temperature does not show any detectable effect on the reaction. Another important factor affecting the equilibrium is the monomer concentration. Since the forward reaction is bimolecular and the reverse reaction is unimolecular, increasing the monomer concentration favors the forward reaction [5].

Two factors are critical in producing high molecular weight polyamic acid: sequence of adding monomer and stoichiometry. Stoichiometry is the key to achieve high molecular weight in all condensation polymerizations. A strict molar ratio of dianhydride and diamine added to the synthesis system is demanded, as close as possible, to obtain high molecular weight polyimide [6]. Previous research has shown that the sequence of adding

monomer into the synthesis system plays an important role in polymer chain growth. Adding solid dianhydrides into a diamine solution results in the higher molecular weight polyamic acid than any other possible sequence. It is believed that because dianhydrides are more active than diamines, the former is more likely to react with impurities in the solution than the latter. By slowly dissolving dianhydrides into the diamine solution, the small amount of dianhydride dissolved in the solution has a much higher possibility to react with diamine than with any impurities and, thus, a better stoichiometry is maintained. For the same reason, dianhydride might be added slightly in excess (less than 1%) to produce high molecular weight polyamic acid [6].

2.1.2 Thermal imidization of polyamic acid

The intermediate polyamic acid is usually converted to the polyimide by thermal imidization. There are two different routes: bulk thermal imidization and solution thermal imidization. Bulk thermal imidization is especially useful when the polyimide does not dissolve in the polar aprotic solvent and the final product is desired in a film or a coating form. Films are first cast and then taken through a thermal cycle with the temperature ranging from 100°C to 350°C to achieve dry films with close to 100% imidization

It is important to recognize that there are complicating factors involved in this seemingly simple process, which finally determine the degree of imidization of the polyimide products. The rate of imidization is usually fast in the initial stage due to the presence of the solvent and, thus, good chain mobility. In the later stages of the reaction, the rate

decreases because of the loss of the residual solvent and the increase of the Tg and, thus, deceased chain mobility [7].

Solution thermal imidization is used when the polyimide is soluble in the polar aprotic solvent and the final product is desired as powder. A second solvent is used and the mixture is heated to 180°C-220°C. The commonly utilized solvents are o-dichlorobenzene, m-cresol and dipolar aprotic amide solvents. Water produced from the imidization reaction forms a low boiling point azeotrope with the solvents which is distilled off from the system. The kinetics studies show that at the early stage of the imidization, the molecular weight of the polymers in the system decreases due to the reverse reaction of the polyamic acid at high temperature and the polyamic acid degradation caused by water. As the reaction continues, the molecular weight starts to increase and continues to increase even after the imidization degree approaches 100% [7].

2.1.3Chemical imidization of polyamic acid

The chemical imidization of polyamic acid requires ambient conditions compared to solution thermal imidizaton. The process essentially consists of treating the polyamic acid with a mixture of aliphatic carboxylic acid anhydride and tertiary amine at ambient temperatures. The common reagents utilized are acetic anhydride, pyridine or triethylamine.

The mechanism of the chemical imidization involves reaction of the tertiary amine with an anhydride, which is more susceptible to nucleophilic attack. It has been stated that the reverse propagation reaction characteristic of the thermal imidization does not occur in chemical imidization. However, chemical imidization may lead to a substantially higher percentage of isoimide moieties in the final product, which at higher temperature converts to the more stable imide (Figure 2.2). In general, the chemical imidization technique requires a final treatment where the polyimide powder is heated briefly to 300°C (or >Tg) to complete imidization, remove trace of solvents, and convert possible isomers [8, 9, 10].

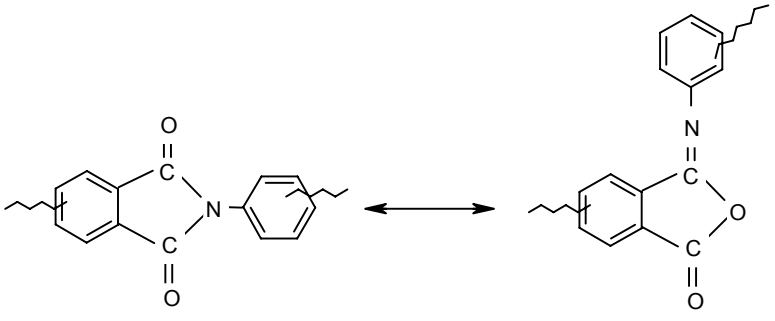

Figure 2.2 Conversion between polyimide and polyisoimide

2.2 One-step high temperature solution polymerization

This technique is essentially the combination of polyamic acid formation and solution thermal imidization in one–step [11]. The high temperature process is often performed in the presence of catalysts such as quinoline, tertiary amines, alkali metals and zinc salts of carboxylic acids. It is especially useful for polymerization involving non-reactive

dianhydrides or diamines. An interesting feature of this method is that it often yields polyimides with a higher degree of crystallinity than what could be obtained with two-step method [5].

2.3 Effect of imidization method on properties of polyimides

Previous studies show that for some polyimides, thermal imidization in the condensed state results in fragile and insoluble materials. However, this drawback can be overcome if chemically induced processes are used instead at room temperature [1, 2]. The property differences in the films synthesized by different imidization processes have also been studied. The films thermally imidized in the condensed state tend to have better chain packing than those chemically imidized. It is likely that the high temperature during the thermal imidization process facilitates better molecular ordering [1, 3].

Using chemical imidization at ambient temperature may be hard to achieve complete imidization [14]. The chemical imidization technique usually requires a final treatment in which the polyimide powder is heated briefly to temperatures near 300°C to complete the imidization and remove traces of any solvents. Imidization degree is another important factor that affects polyimide material properties. Earlier studies have reported that the physical properties, Tg, film density, of polyimide films vary with their imidization degree. The CO_2 sorption and permeation of the films also change with imidization degree [15].

In this study, because of the thermal sensitivity of DABA and the preference of powder for further treatment, we will utilize both chemical and solution thermal imidization. The physical and transport properties of polyimide membranes from these two imidization processes will be compared.

2.4 Covalent crosslinking

Crosslinking is an important tool to resist the swelling by the feed penetrants and to improve membrane performance. However, most of the crosslinking methods reported involve procedures that would be difficult to apply in commercial membrane manufacturing processes. A new approach for crosslinking has been demonstrated to be effective in the suppression of CO_2 plasticization. It is a post-treatment that could be added to the existing membrane and maintain the hollow fiber morphology with a mild processing temperature. It is based on the idea of crosslinking the carboxylic acid groups with multi-functional alcohols. Another advantage of this method is that the number of crosslinkable sites could be controlled stoichiometrically in synthesis, and therefore, is reproducible [16].

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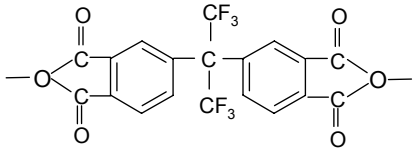
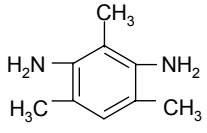
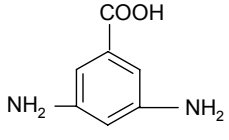
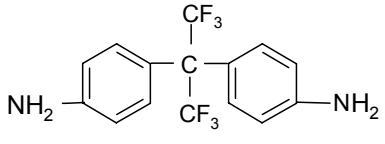
Chapter 3 Experimental Procedures

3.1 Materials

3.1.1 Monomers

All the polyimides used in this study were synthesized in our lab. The monomers used in the synthesis are shown in Table 3.1 along with their chemical structure and sources

Table 3.1 Monomer structure and source

Monomer	Chemical structure	Source
4, 4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)		Lancaster
4, 6-trimethyl-1, 3-phenylendiamine (DAM)		Aldridge
3, 5-diaminobenzoic acid (DABA)		Aldridge
4, 4'-(hexafluoroisopropylidene) dianiline (6FpDA)		Aldridge

3.1.2 Other chemicals

All the other chemicals employed this study were used as received unless further stated. The purity and source of the solvents are listed in Table 3.2.

Table 3.2 Solvent Purity and Source

Solvent	Purity	Source
toluene	99.5% ACS spectrophotometric grade	Aldridge
2, 2, 4-trimethylpentane (iso-octane)	99+% ACS spectrophotometric grade	Aldridge
N-methyl-2-pyrollidone (NMP)	99.5% anhydrous	Aldridge
tetrahydrofuran (THF)	HPLC	Fisher-Scientific
o-dichlorobenzene (DCB)	99%	Aldridge
aectone-deuterated	99.9%	Cambridge Isotope Laboratories Inc
chloroform-deuterated	99.9%	Cambridge Isotope Laboratories Inc
triethylamine	99%	Aldridge
acetic anhydride	98% ACS reagent	Aldridge
p-toluenesulfonic acid monohydrate (PTSA)	99%	ACROS
(trimethylsilyl)diazomethane	2.0M solution in hexane	Aldridge
dichloromethane	99%	Aldridge
aluminum acetylacetonate	99%	Aldridge

3.2 Polyimide synthesis

All the polyimides used in this study were synthesized with the 'two-step' method: formation of polyamic acid and imidization [1]. The imidization step was carried out by both the chemical and thermal methods.

3.2.1 Synthesis of polyamic acid

6FDA and DAM monomers were purified by sublimation. The diamines were poured into a thoroughly torch-dried 100 ml three-neck flask containing a magnetic stir bar, and a small amount of solvent, N-methyl-2-pyrollidone (NMP) dried over molecular sieves, was transferred into the flask through a solvent line. After the diamines were completely dissolved, a stoichiometric amount of dianhydride was added. More NMP was added until the solution concentration was ~15% based on monomer weight. The polymerization reaction was carried out at room temperature for at least 12 hours to give a viscous polyamic acid solution.

3.2.2 Chemical imidization

The polyamic acid solution obtained from the above procedure was diluted to ~5% with additional NMP. Chemical imidization was carried out with a four-time excess amount of acetic anhydride and triethylamine at 100°C for one hour. The entire synthesis vessel was constantly purged with dry nitrogen. The stoichiometry of the polyamic acid formation and the chemical imidization is shown in Appendix VII.

3.2.3 Thermal imidization

A certain amount of o-dichlorobenzene (DCB) dried over molecular sieves was added to the 15% polyamic acid solution to create a 4:1 volume ratio of NMP and DCB. The solution was then heated to 180°C for 24 hours in a constantly stirred N_2 purged atmosphere. Water produced during the cyclodehydration of the polyamic acid formed a low boiling point azeotrope with DCB and NMP, which was subsequently distilled out of the reaction solution with a Dean-Stark trap. Fresh DCB was added into the solution continuously to maintain a constant concentration.

3.2.4 Polyimide precipitation

The final polyimide solution was cooled and poured into methanol where the precipitate was soaked in methanol for 12 hours. Polyimide was collected by filtration, blended and dried at 100°C in vacuum for 24 hours.

3.3 Film formation

Polyimide membranes without DABA were prepared by casting 5 wt% dichloromethane solutions in a metal ring sitting on a glass plate to give a homogeneous dense film, as confirmed by density measurements. Because of the change in polarity caused by introducing DABA units, polyimides were dissolved in tetrahydrofuran to achieve easier dissolution. Solutions containing 5 wt% of the polyimide were cast on Teflon plates. All the cast membranes were dried further at 60˚C in vacuum for 24 hours after an initial drying in air and at room temperature.

3.4 Covalent crosslinking

Vacuum-dried DABA containing polyimide and p-toluenesulfonic acid monohydrate (PTSA) with a COOH/AlAcAc mole ratio of ~0.05 were added into a torch-dried flask with magnetic stirring and nitrogen purge. Pre-dried NMP was transferred into the flask to make a ~10% solution. A one hundred-time excess amount of ethylene glycol was added and the system was heated to 140°C for 18 hours with a condenser. The polymer was precipitated and the mono-ester films were cast. The cast films were dried in vacuum oven at 220°C for a certain time ranging from 2 hours to 24 hours to achieve the final crosslinking. The stoichiometry of the ethylene glycol mono-esterification is described in Appendix VII.

*3.*5 Pervaporation

The PV experiments were performed in an apparatus developed in this laboratory. The scheme of the apparatus is shown in Figure 3.1. The pervaporation measurements reported here were conducted at 100°C. The effective membrane area was 38 cm^2. The downstream pressure was maintained below 10 mm Hg. Since the vapor pressures of toluene and iso-octane at 100 °C are 556 torr and 451 torr, respectively, the maximum downstream vapor activity was always 0.02 or less. Steady state permeation was typically obtained after 3-8 hours of operation for the polymers with penetrants and film thicknesses used here. The flux was measured by weighing the penetrants collected by a liquid nitrogen trap in the downstream line during a given amount of time. The composition of penetrant collected was analyzed by measuring the refractive index of the

binary hydrocarbon mixture with a Fisher ABBE-3L refractometer. The calibration accuracy is ±0.1 wt% of toluene concentration [2]. The results from refractive index measurements compare well with those from gas chromatography.

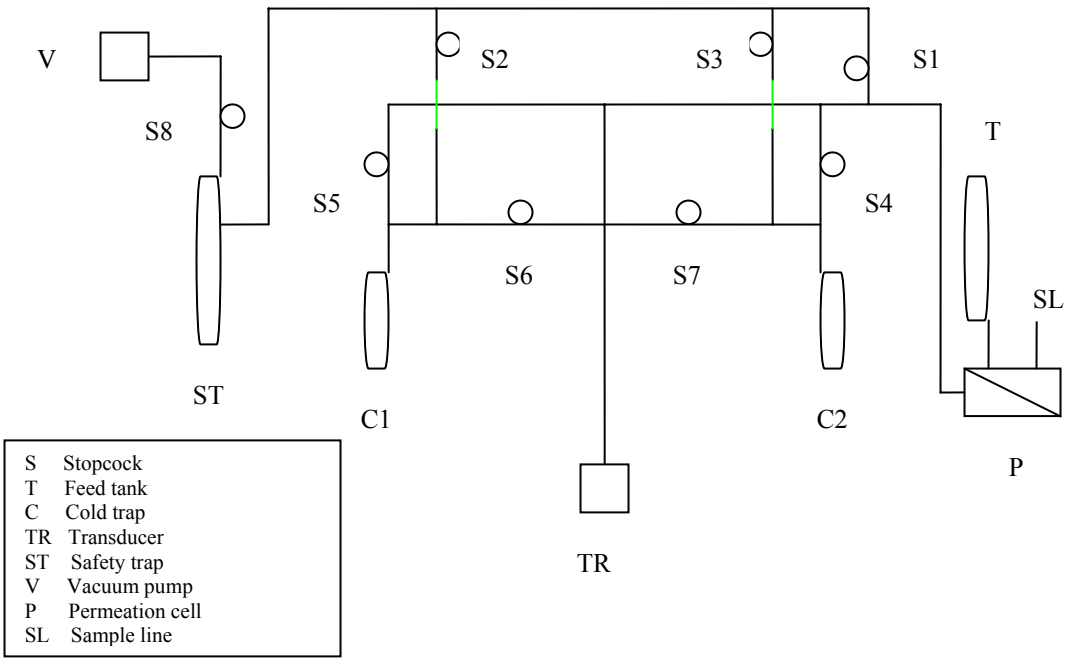


Figure 3.1 Scheme of pervaporation apparatus

3.6 Sorption

The equilibrium sorption of the feed mixture in the membrane was determined as follows. Precisely weighed dry membranes sheets (about 0.1 g each) were immersed into a toluene/iso-octane mixture at 100°C for 24 hours to reach equilibrium, then removed, wiped quickly with a Kim-Wipe and transferred to a weighing bottle. To correct for the evaporation of liquid during the transfer, the membrane weight was measured as a

function of time using a microbalance, and then extrapolated to zero time to obtain the original weight of the wet membrane. The evaporation of the liquid during the transfer step was always less than 2 wt% of the total amount of liquid in the membrane.

The composition of the toluene/iso-octane mixture sorbed in the membrane, when in equilibrium with a feed mixture of given composition, was determined in the following way. A membrane sheet (about 0.02g as dry weight) that had been equilibrated with a toluene/iso-octane mixture was transferred into a sample vial containing 1 ml NMP. The vial was capped and kept at room temperature for 12 hours for membrane dissolution and equilibration between the vapor and the liquid. The vapor phase in the vial was analyzed using a HP 5890A gas chromatograph equipped with a SUPELCOWAX™10 Capillary Column with 30m x0.32 mm x 0.25 μm dimension. A calibration was constructed from a series of standards between the GC-detected peak areas for toluene/iso-octane in the vapor phase and the amount of the liquid toluene/iso-octane in the standards. This calibration was used to determine the composition of the toluene/iso-octane liquid in the membrane. The deviation for replicate experiments was less than 6%. Therefore, the error in solubility selectivity calculated from the sorption results is within 12%.

3.7 Polymer characterization

Molecular weight distributions of the polyimide materials were measured by a Waters GPC calibrated with polystyrene standards. The carboxylic acid in the polyimides is masked by (trimethylsilyl)diazomethane before GPC tests. The masking process is

described in details in Appendix IV. The density of each dry polymer film was measured using a gradient density column based on aqueous calcium nitrate solutions at 23°C. Thermal analysis was performed using a Perkin-Elmer DSC 7 at a heating rate of 20°C/min. Wide angle X-ray diffraction (WAXD) was employed using a Philips PW 1720 X-ray generator with CuKα_1 radiation of wavelength 1.54Å at 40kV and 20mA. Fourier transformed infrared spectra (FTIR) of thin polyimide films were obtained with a Mattson Infinity Gold FTIR with 2 cm^{-1} resolution. The density, DSC, WAXD and FTIR measurements of the polyimide samples in this study were made after pervaporation tests and vacuum drying. Nuclear Magnet Resonance (NMR) analysis was recorded on a Varian Inova-500 spectrometer at a resonance frequency of 499.352 MHz for ^{1}H and 125.705 Hz for ^{13}C with 10% polyimide solutions in chloroform-d or acetone-d_6 at 27°C.

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Chapter 4 Background and Theory

4.1 Parameters for pervaporation performance

Pervaporation is usually characterized by two major measurable quantities: permeation rate and selectivity. The former is usually expressed in terms of the flux normalized by the membrane thickness (l·flux); the dry membrane thickness is typically used [1]

$$l \cdot flux_i = \frac{l \cdot Permeation\ mass\ of\ component\ i}{Membrane\ area \cdot permeation\ time} \tag{1}$$

where l is the membrane thickness. Pervaporation selectivity is usually defined as

$$\alpha_{perv} = \frac{y_i / y_j}{x_i / x_j} \tag{2}$$

where x, y are mole or weight fraction in the upstream feed and the downstream permeate respectively, and i, j refer to the components being separated, e.g., toluene and iso-octane. While this gives a pragmatic view of system performance, other more fundamental definitions might also be used as explained in the appendix.

According to the solution-diffusion model, the selectivity of a membrane is factored into a product of solubility selectivity and diffusivity selectivity; however, this can only be written in simple unambiguous forms when the sorption and transport processes are described by linear relations. A pervaporation solubility selectivity α_S can be defined from equilibrium sorption results as followings

$$\alpha_S = \frac{x_{im} / x_{jm}}{x_{if} / x_{jf}} \tag{3}$$

where m refers to the membrane phase and f refers to the liquid feed mixtures. The diffusivity selectivity α_D would then be the following

$$\alpha_D = \frac{\alpha_{perv}}{\alpha_S} \tag{4}$$

The solution and diffusion of penetrants in the pervaporation experiments are strongly affected by polymer/penetrant interactions. Due to the plasticization of the polymer by each penetrant, the gradient of each penetrant may be affected by the gradient of other penetrants. In addition, the solubility selectivity defined above describes the sorption equilibrium between liquid feed and the membrane immediately adjacent to it, while the diffusivity selectivity calculated from equation (4) represents an average of the diffusivity characteristics across the membrane.

4.2 Parameters for the membrane material properties

Polymers used to form pervaporation membranes can be characterized by fundamental measures of cohesive energy and chain packing (in the absence of perturbations caused by the penetrants) like the solubility parameter, fractional free volume, or the wide angle X-ray diffraction d-spacing. Some of the responses observed in this study will be discussed in terms of these basic characteristics of the neat polymer. The solubility parameter, δ, represents one of the simplest approaches to characterize the inter-chain force field and to predict polymer/solvent interactions. The solubility parameter of a

polymer is largely determined by its chemical structure and can be estimated by group contribution methods [2]. As a general rule, the solubility of a polymer in a given solvent is most favored when the solubility parameters of the polymer and the solvent are similar in magnitude.

Fractional free volume (FFV) can be defined as follows

$$FFV = \frac{V_T - V_0}{V_T} \tag{5}$$

where V_T is the specific volume of the polymer membrane at temperature T and can be calculated from the experimental film density. The occupied volume at 0 K, $V_{0,}$ can be estimated by Bondi's method:

$$V_0 \approx 1.3 V_W \tag{6}$$

where V_W is the van der Waals volume and can be calculated by group contribution methods[2]. The FFV is a measure of average chain packing, which to some extent is influenced by chain architecture and chain flexibility [3]. The calculation of solubility parameter and fractional free volume of the polyimide membranes involved in this study is described in detail in Appendix VII.

One consequence of a significant degree of liquid sorption is plasticization of the polymer membrane and the corresponding reduction in the glass transition temperature. The membrane at the upstream surface is highly swollen while that at the downstream side is nearly in the dry state; thus, there is a distribution of glass transition temperatures

across the thickness of the membrane. The glass transition temperature of a swollen membrane can be estimated by the Fox equation [4].

$$\frac{1}{T_{gM}} = \frac{w_m}{T_{gm}} + \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \cdots\cdots \quad (7)$$

where T_{gM}, T_{gm} and T_{g1} are the glass transition temperatures of the swollen membrane, the dry membrane, and penetrant 1, etc while w_m is the weight fraction of polymer, and w_1 and w_2 are the weight fraction of penetrants in the swollen membrane. The glass transition temperatures of many organic solvents have been determined [5]; the value for toluene is 117 K while that for iso-octane is 98 K.

4.3 Material structure and transport relations

The relationships between polymer structure and gas permeation properties have been extensively investigated to understand current materials and predict new material performance. As a general rule, the solubility of a series of gases in a given polymer correlates with the condensability of the penetrant, which can be characterized in terms of its critical temperature, boiling point, etc [6]. The diffusivity of gases in polymers is mainly controlled by the shape and size of the penetrants and the free volume of the polymer. Thus, one could use differences in polymer-penetrant interactions to achieve high solubility selectivity, though the interactions are weak for most gases, or by tuning material structure (mainly chain stiffness and intersegmental packing) to obtain high diffusivity selectivity. For polyimide materials, solubility has been correlated with their wide angle X-ray diffraction (WAXD) d-spacing and fractional free volume. The

diffusivity of a given penetrant shows reasonably good correlation with the polymer fractional free volume or solubility parameter [3].

Few studies of structure/transport relations have been reported for pervaporation because of the complex behavior resulting from the strong polymer/penetrant interactions. However, the understanding of polyimide materials already established from extensive gas permeation studies provides an excellent starting point for understanding pervaporation. In this study, the structure/transport relations for DABA containing polyimide materials in pervaporation will be viewed with a similar framework as used for gas permeation.

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Chapter 5 Transport of Chemical Imidized 6FDA-DAM/DABA Membranes

In this chapter synthesis of a series of 6FDA-DAM/DABA materials is base on the chemical imidization method as described in Chapter 3. The chemical structure of the 6FDA-DAM/DABA materials is shown in Figure 5.1. The structure and composition were verified by NMR, UV-Visible and FTIR spectroscopy, which will be discussed in chapter 7. The pervaporation and sorption properties of these polyimides in toluene/iso-octane mixtures were tested. Pervaporation flux and selectivity depend on the structure of the membrane material, feed composition, temperature and downstream pressure; however, temperature and downstream pressure were held constant in this study in order to focus on the effects of polymer structure and feed composition on pervaporation performance.

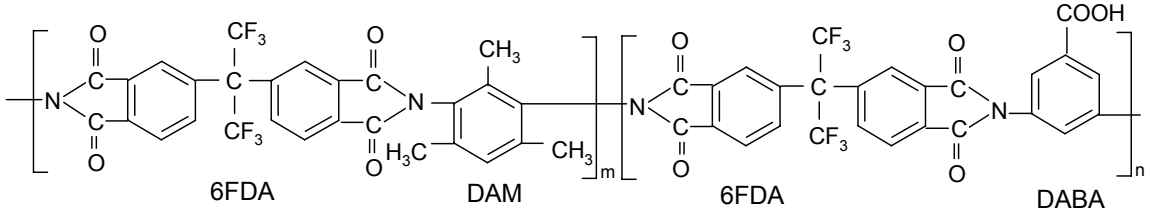


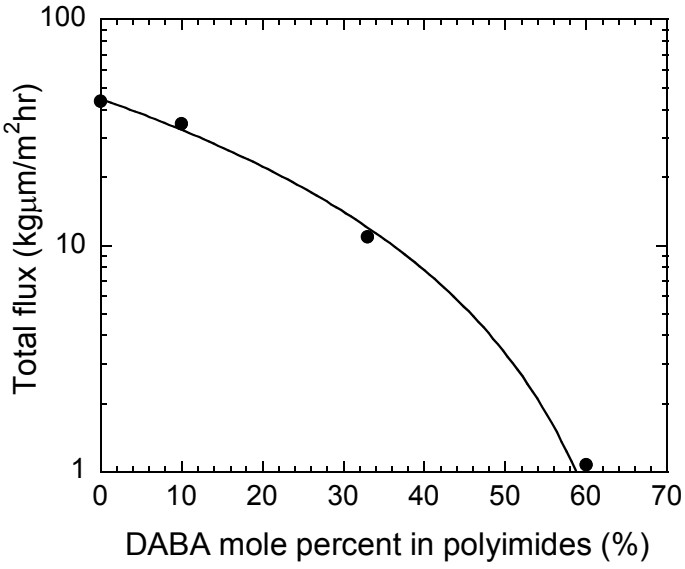
Figure 5.1 Structure of the polyimide materials used in this study. The notation used here is illustrated by 6FDA-DAM/DABA(33%) for the case where m = 2, n = 1

5.1 Pervaporation Performance

5.1.1 Effect of DABA Content

The flux and selectivity properties of polyimide materials containing different contents of DABA were measured using a feed containing 50/50wt% toluene/iso-octane with the results shown in Figure 5.2. The normalized total flux decreases while the selectivity for toluene over iso-octane increases as the DABA content increases in nearly linear ways for the semi-logarithmic scales used in both parts of Figure 5.2.

Figure 5.3 shows the pervaporation selectivity partitioned into its solubility and diffusivity components, determined by equation 4.3 and equation 4.4, as a function of the DABA content of the polyimides for a 50/50 toluene/iso-octane feed. Both the solubility and the diffusivity selectivity increases with DABA content. The increase in diffusivity selectivity is exponential while that in solubility selectivity is linear in DABA content. Thus, increasing DABA content has a more significant impact on diffusivity selectivity than solubility selectivity. The material with low DABA content has both solubility selectivity and diffusivity selectivity of about the same magnitude; while the materials containing a high DABA content, the diffusivity selectivity dominates the total pervaporation selectivity.



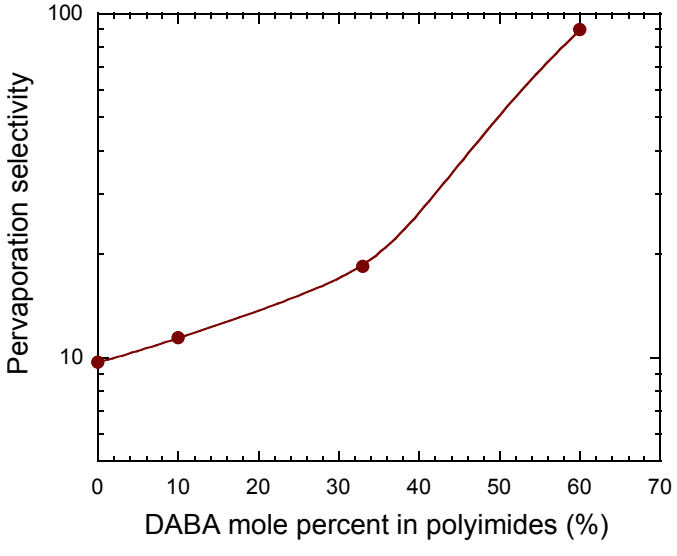


Figure 5.2 Pervaporation performance of polyimides with different DABA contents for a 50 wt% toluene/iso-octane feed at 100°C: (top) normalized total flux (toluene plus iso octane as defined by equation 4.1 in the text) (bottom) pervaporation selectivity for toluene versus iso-octane as defined by equation 4.2

As DABA groups are added, the polymer becomes more polar. Since toluene and iso-octane are both non-polar, the swelling of the membrane by both toluene and iso-octane is reduced. However, toluene is more polarizable and has a higher solubility parameter than iso-octane; thus, adding DABA makes the polymer more sorption selective for toluene over iso-octane. Table 1 shows that the inherent film density of the polyimides increases significantly with increasing DABA content, while the molecular weight of each repeat unit is essentially constant (676 Daltons for 6FDA-DAM vs. 674 Daltons for 6FDA-DABA repeat unit). Therefore, the chain packing of the polyimide membranes is facilitated by the interaction between the DABA groups, most likely caused by the hydrogen bonding between the carboxylic acids. By making the polyimide chains more well-packed, the absolute rates of permeation of both iso-octane and toluene become slower. Nevertheless, the transport rate of the larger iso-octane molecules is slowed more than that of toluene; thus, the diffusivity selectivity improves. In summary, the flux decreases and pervaporation selectivity increases as the content of DABA groups in these polyimide membranes.

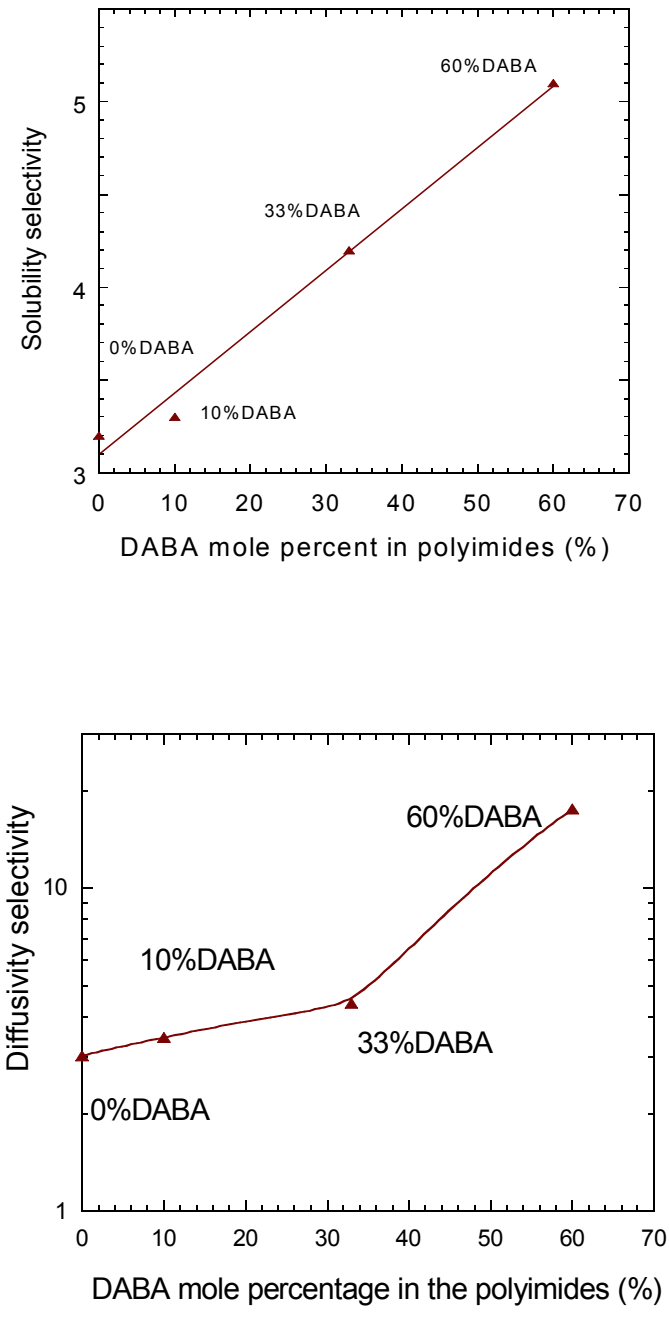


Figure 5.3 Solubility selectivity (top) and diffusivity selectivity (bottom), as defined by equation 4.3 and equation 4.4 for toluene over iso-octane of polyimides with different DABA contents for a 50 wt% toluene/iso-octane feed at 100°C

Table 5.1 Physical properties of polyimides and penetrants

Polyimides or penetrants	Tg (°C)	Solubility parameter δ $(J/cm^3)^{1/2}$	Fractional free volume	Polymer film density (g/cm^3)
6FDA-DAM	339	26.4	0.190	1.338
6FDA-DAM/DABA(10%)	382	26.7	0.189	1.350
6FDA-DAM/DABA(33%)	379	27.3	0.184	1.380
6FDA-DAM/DABA(60%)	-	28.0	0.180	1.414
Toluene	-	18.2	-	-
Iso-octane	-	14.1	-	-

5.1.2 Effect of Feed composition

Figure 5.4 shows the effect of the composition of the toluene/iso-octane feed on the pervaporation performance for polyimide membranes containing various amounts of DABA. Figure 5.4(top) shows the total (toluene plus iso-octane) flux normalized by their thickness while Figure 5.4(bottom) shows the pervaporation selectivity of toluene/iso-octane as defined by equation 4.2. For each of the materials with a given DABA composition in the polymer, flux increases and selectivity decreases rapidly as the amount of toluene in the feed increases.

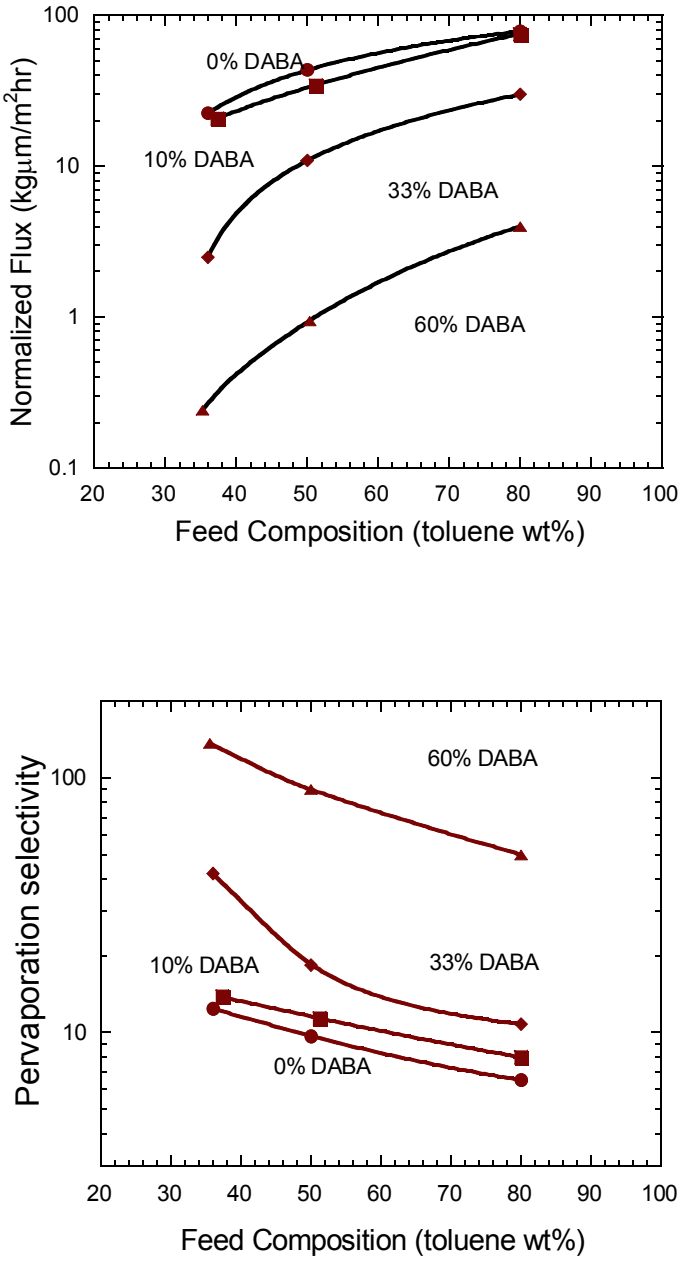


Figure 5.4 Pervaporation performance of polyimide materials with different DABA content versus toluene/iso-octane composition feed: (top)normalized total flux, and (bottom)pervaporation selectivity for toluene over iso-octane.

Figure 5.5 shows the solubility and diffusivity selectivity for the 6FDA-DAM/DABA (33%) membrane as a function of feed composition. At high toluene concentrations in the feed, both the solubility and the diffusivity selectivity are greatly decreased. The decay of diffusivity selectivity is more extreme than that of solubility selectivity. To illustrate the feed composition effect more clearly, the total permeability and the permeability for each component versus feed composition are shown in Figure 5.6 for the 6FDA-DAM/DABA (33%) membrane. Permeability is defined by equation 2 in Appendix I. The permeabilities of both toluene and iso-octane increase rapidly as the toluene percentage in the feed increases. If the penetrant-membrane interactions were weak, the permeability should be a constant independent of feed composition because unlike the flux, the permeability is normalized by the driving force for permeation. However, because of the strong plasticization of the membrane material by toluene, the permeability of each component increases significantly as the toluene content of the feed increases. The interactions between the DABA groups are not strong enough to entirely suppress the large swelling and subsequent plasticization by toluene, as might be expected. Plasticization decreases diffusivity selectivity more than it does the solubility selectivity.

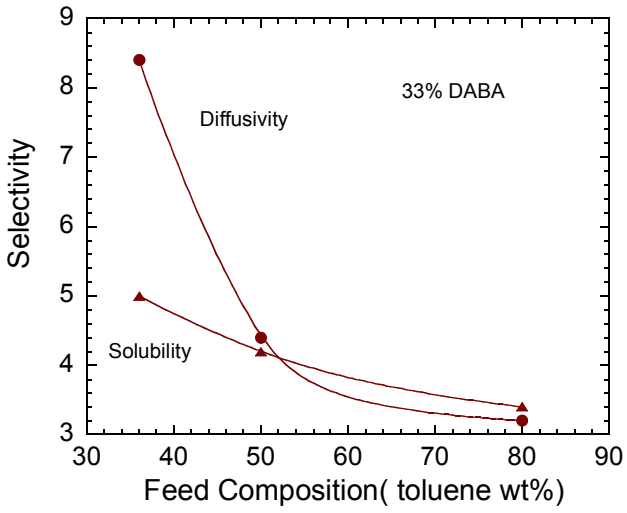


Figure 5.5 Solubility and diffusivity selectivity at 100°C for toluene over iso-octane for the 6FDA-DAM/DABA(33%) membrane as a function of the toluene/iso-octane feed

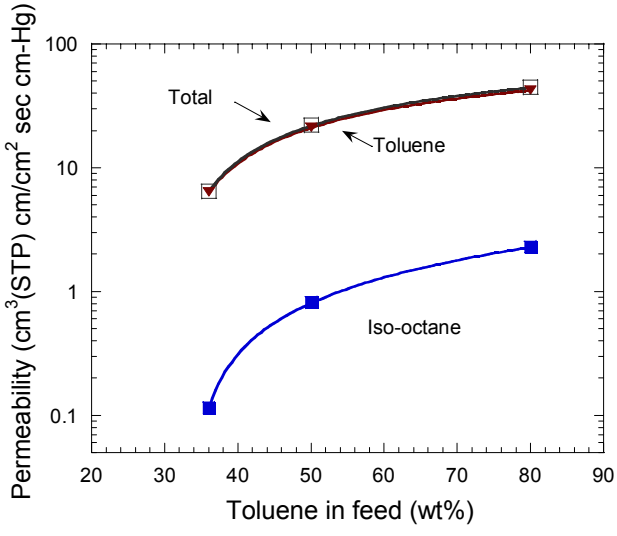


Figure 5.6 Permeability coefficients, as defined by equation 2 in appendix, at 100°C for the 6FDA-DAM/DABA(33%) membrane as a function of toluene/iso-octane feed composition

5.2 Membrane swelling in toluene/iso-octane mixtures

To better understand the effects of the DABA content of the polyimide materials and of the toluene composition in the feed on pervaporation performance shown above, swelling and sorption tests were conducted. The swelling of 6FDA-DAM/DABA(10%) and 6FDA-DAM/DABA(33%) membranes for different feed compositions is illustrated in Figure 5.7. The swelling of the 33% DABA material by toluene and by iso-octane for the same feed composition is reduced compared to that in the 10% DABA material. The toluene swelling of both materials increases significantly as the toluene content increases in the feed. The iso-octane swelling increases rapidly initially, and then more slowly as the iso-octane content in the feed increases. The swelling results agree with the pervaporation performance discussed earlier. For a given toluene/iso-octane feed, addition of DABA groups reduces the swelling of the membrane by both toluene and iso-octane in the membrane, and improves the solubility selectivity. However, the DABA groups do not entirely suppress the plasticization when the toluene content in the feed is high.

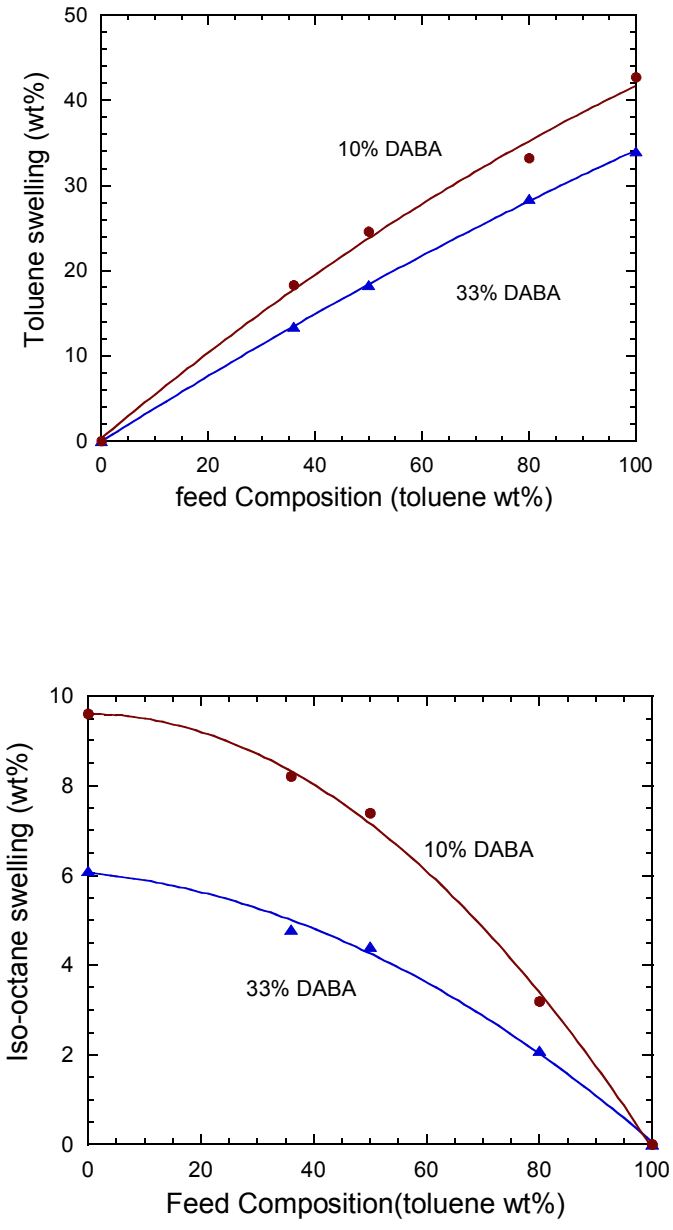


Figure 5.7 Swelling of polyimides in toluene/iso-octane mixtures at 100°C (top) toluene swelling, (bottom) iso-octane swelling of 6FDA-AM/DABA(10%) and 6FDA-DAM-DABA(33%) membranes in toluene/iso-octane mixtures at 100°C

The plasticization of the membrane resulting from the swelling by toluene and iso-octane results in a reduction in the glass transition temperature of the swollen polyimide membrane. Using the sorption results in Figure 5.7, the glass transition temperatures of a 6FDA-DAM/DABA (33%) membrane, calculated using equation 4.7, equilibrated with various feed mixtures at 100°C is shown in Figure 5.8. Even the small amount of pure iso-octane reduces the glass transition temperature of the membrane by 160°C. As the membrane swelling increases with increased toluene presence in the feed, the glass transition temperature of these membranes continues to decrease. In pure toluene at 100°C, the glass transition temperature of this polyimide is reduced to essentially room temperature, even though that of the dry membrane is 379°C. However, because of the concentration gradient in the membrane during the pervaporation process, the glass transition temperature or the degree of plasticization across the membrane varies. The membrane layer next to the liquid feed should correspond to the calculated value shown in Figure 5.7 while the membrane layer adjacent to the downstream vacuum is essentially in the dry state and should have the glass transition temperature of the dry polyimide. Figure 5.8 suggests that when the membrane exposed to a feed containing more than 40% toluene, the glass transition temperature of a portion of the membrane on the upstream side is below the operation temperature (100°C), i.e., only the downstream portion of the membrane is in the glassy state.

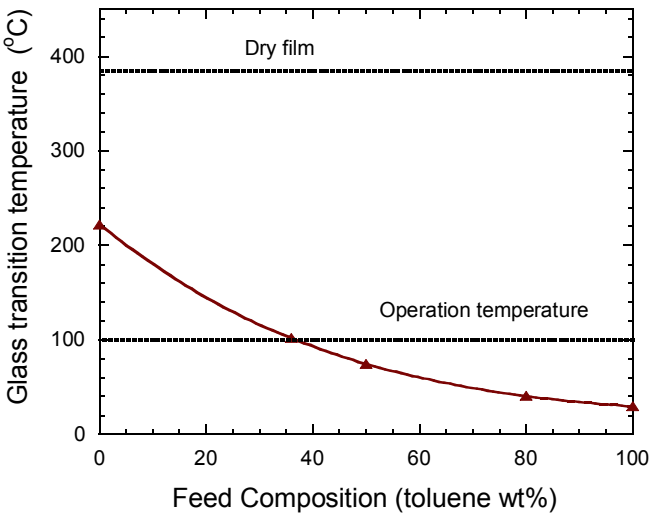


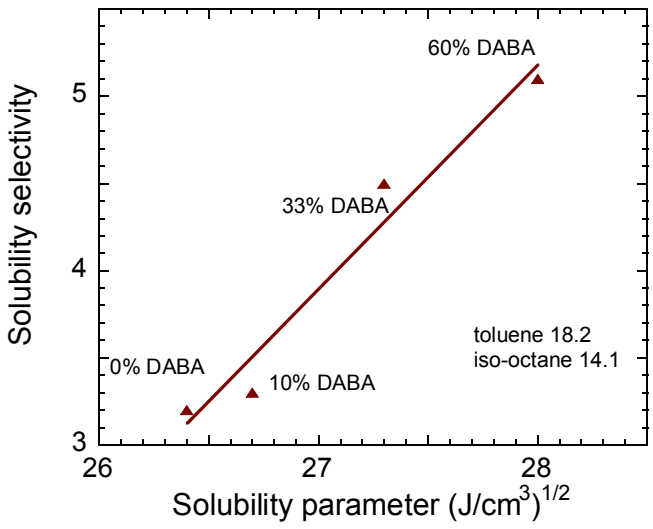
Figure 5.8 Glass transition temperatures for the 6FDA-DAM/DABA(33%) membrane in swelling equilibrium at 100°C with toluene/iso-octane feed as calculated by the Fox equation using data in Figure 5.7

5.3 Structure-transport relations

Although very approximate, the difference between the solubility parameters of a given polymer and a given penetrant provides a first order measure of the polymer-penetrant interaction in gas permeation [1]. Therefore, for a given polymer, solubility parameters can provide a useful correlating scheme for solubility selectivity; the penetrant with a solubility parameter similar to that of the polymer should be more selectively sorbed by the polymer. Figure 5.9(top) shows that the solubility selectivity of these polyimide membranes increases as the solubility parameter of the membranes increases. The solubility parameters for toluene and iso-octane are 18.2 and 14.1$(J/cm^3)^{1/2}$ [2], respectively. As the solubility parameter of the polymer, δ_p, increases, the relative affinity

of the membrane for toluene compared to iso-octane improves as may be seen from examining the ratio (δ_p -18.2)/(δ_p -14.1). Based on gas permeation studies, the diffusivity selectivity might be expected to correlate with the polymer fractional free volume [1]. The fractional free volume can be easily calculated for penetrant-free membranes using group contribution methods as discussed in Chapter 4. In gas permeation, the fractional free volume of a pure polymer is an appropriate parameter since most gases show very low solubility in the membrane. In pervaporation, the swelling and plasticization of the membrane by the penetrants can be very significant as shown in Figure 5.7 and Figure 5.8; thus, the fractional free volume would be significantly increased by such swelling. Nevertheless, transport models show that the membrane layer close to the downstream side is nearly in the dry state [2], so it can be argued that it is this part of the membrane that *effectively controls the relative diffusion through the whole membrane*. Thus, the concept of fractional free volume in the dry membrane may still have great relevance in pervaporation. This expectation provides an important connection between gas separation performance and pervaporation performance.

For the same reason, the diffusivity selectivity of pervaporation difined by Equation 4.4, as an average of diffusivity characteristics across the membrane, can be explained as the effective diffusivity selectivity, contributed mainly by the relatively dry membrane layer close to the downstream side.



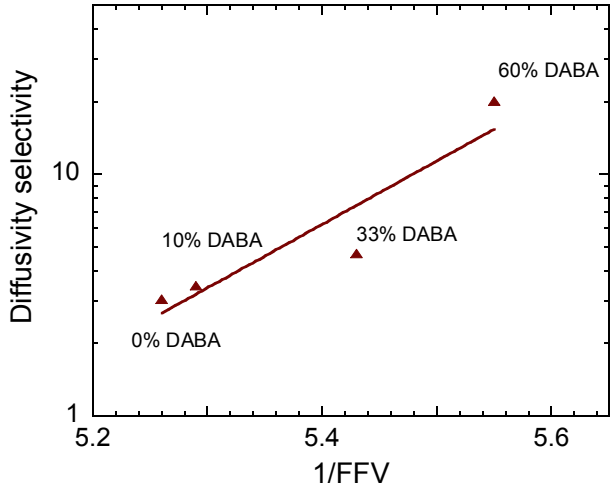


Figure 5.9 Correlation of mass transport behavior with material properties: (top) solubility selectivity correlated with solubility parameter, (bottom) diffusivity selectivity correlated with fractional free volume at 100°C for a 50/50 toluene/iso-octane mixture

Addition of DABA content to the polyimide structure increases chain packing through strong interaction forces, and the fractional free volume of the polyimides decreases. The diffusivity selectivity of these polyimide materials increases greatly as the DABA content increases as discussed above. Therefore, a tentative correlation between diffusivity selectivity and polymer fractional free volume is shown in Figure 5.9(bottom). The diffusivity selectivity increases *exponentially* with the inverse of fractional free volume similar to what has been observed in gas permeation [1]. This exponential relation indicates that the intrinsic chain packing of the essentially unswollen polyimide plays an important role in the diffusion of penetrants in these materials.

Solubility and diffusivity in a pervaporation membrane is determined by the complicated interplay between multiple factors. Solubility is not simply determined by the solubility parameter while diffusivity is not solely governed by free volume. Thus, other membrane parameters would be needed to reach a general correlation of pervaporation performance. We chose these two parameters based on gas permeation results that are explained well by them. The validity of these relations for pervaporation should be tested for a wider range of materials.

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Chapter 6 Transport Properties of Thermally Imidized 6FDA-DAM/DABA Membranes

The mass transport properties of 6FDA-DAM/DABA polyimides prepared by the chemical imidization process were discussed in Chapter 5. In this chapter, a series of 6FDA-DAM/DABA polyimides synthesized by solutuion thermal imidization are described, and their pervaporation, sorption performance are tested in toluene/iso-octane mixtures at 100ºC. The transport and material properties are compared with the corresponding polymers made by the chemical imidization process.

6.1 Pervaporation performance

6.1.1 Effect of DABA content

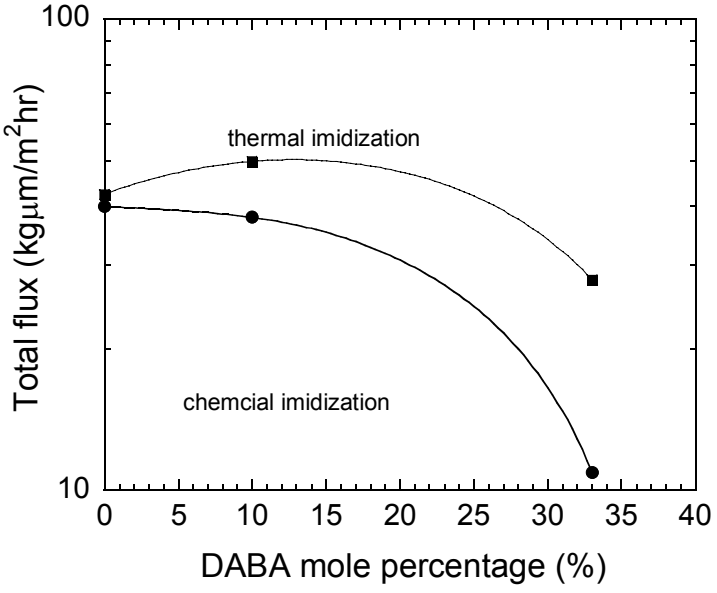
The pervaporation flux and selectivity of the membranes made from 6FDA-DAM/DABA polyimides, containing different DABA contents, synthesized by thermal imidization were measured for a 50/50wt% toluene/iso-octane feed. The results are shown in Figure 6.1.

For the chemically imidized 6FDA-DAM/DABA polyimides, the pervaporation total flux decreases and selectivity increases as the DABA content of the polyimide increases, as discussed in Chapter 5. For the thermally imidized 6FDA-DAM/DABA polyimides, the flux and selectivity of the 6FDA-DAM material are 42 kgμm/m^2hr and 10.4, respectively; while those of 6FDA-DAM/DABA(10%) are 78 kgμm/m^2hr and 8.0,

respectively. The unexpected increase in flux and decrease in selectivity as the DABA content increases from 0% to 10% may be due to the molecular weight issue of the polyimide materials. The molecular weight distributions of the 6FDA-DAM/DABA polyimides used in this study were measured by GPC with conventional calibration, and the results shown in Table 6.1 are molecular weight relative to polystyrene standards. The chemically imidized polyimide series have similar molecular weights. However, for the thermally imidized polyimide series, the molecular weight of 6FDA-DAM/DABA(10%) is significantly higher than that of 6FDA-DAM and 6FDA-DAM/DABA(33%). Higher molecular weight polymer tends to have higher selectivity and lower flux in mass transport [1, 2, 3], which will be discussed later.

Table 6.1 Molecular weights of 6FDA-DAM/DABA polyimides

	chemical imidization		thermal imidization	
	Mn	Mw/Mn	Mn	Mw/Mn
0%	26700	2.8	23900	2.3
10%	26500	1.9	31900	2.6
33%	24500	2.0	26900	2.2



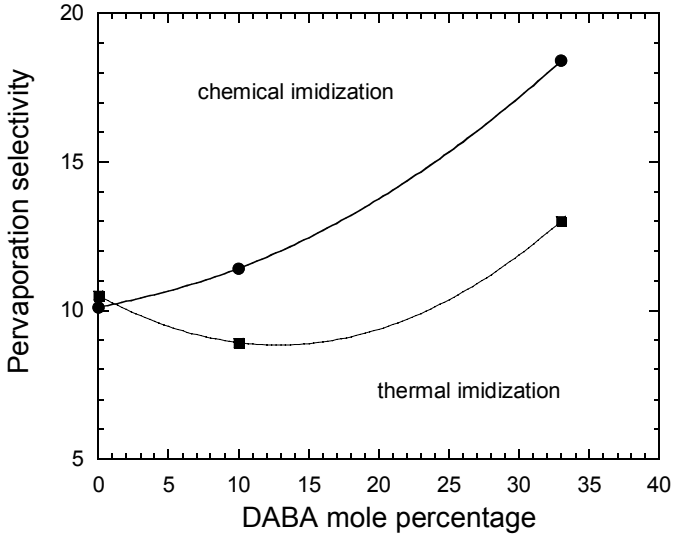


Figure 6.1 Pervaporation performance of membranes made from 6FDA-DAM/DABA polyimides synthesized by the two schemes described in the text for a 50/50 wt% toluene/iso-octane feed at 100°C

The pervaporation selectivity can be partitioned into solubility selectivity and diffusivity selectivity, as shown in Figure 6.2. The solubility selectivity and diffusivity selectivity of the chemically imidized 6FDA-DAM/DABA polyimides both increase as the DABA content in the polymer increases. The solubility selectivity of the thermally imidized polyimides does not change significantly with as the DABA in the polymer increases. The diffusivity selectivity appears to decrease as the DABA content increases from 0% to 10%, then increases significantly as the DABA content increases to 33%. The solubility selectivity and diffusivity selectivity are of about the same magnitude. DABA content has more impact on diffusivity than solubility for the thermally imidized polyimides.

6.1.2 The effect of feed composition

The effect of feed composition was tested at 100ºC with toluene/iso-octane feeds having three different compositions. The results are shown in Figure 6.3. For each material, the pervaporation flux increases and selectivity decreases as the toluene content in the feed increases. The 6FDA-DAM materials imidized by chemical and thermal methods have very close pervaporation performance. However, for the 6FDA-DAM/DABA(10%) and 6FDA-DAM/DABA(33%) materials, chemical imidization and thermal imidization result in different pervaporation performance. The chemically imidized materials have lower flux and higher selectivity than the thermally imidized materials over the whole range of toluene/iso-octane feed compositions.

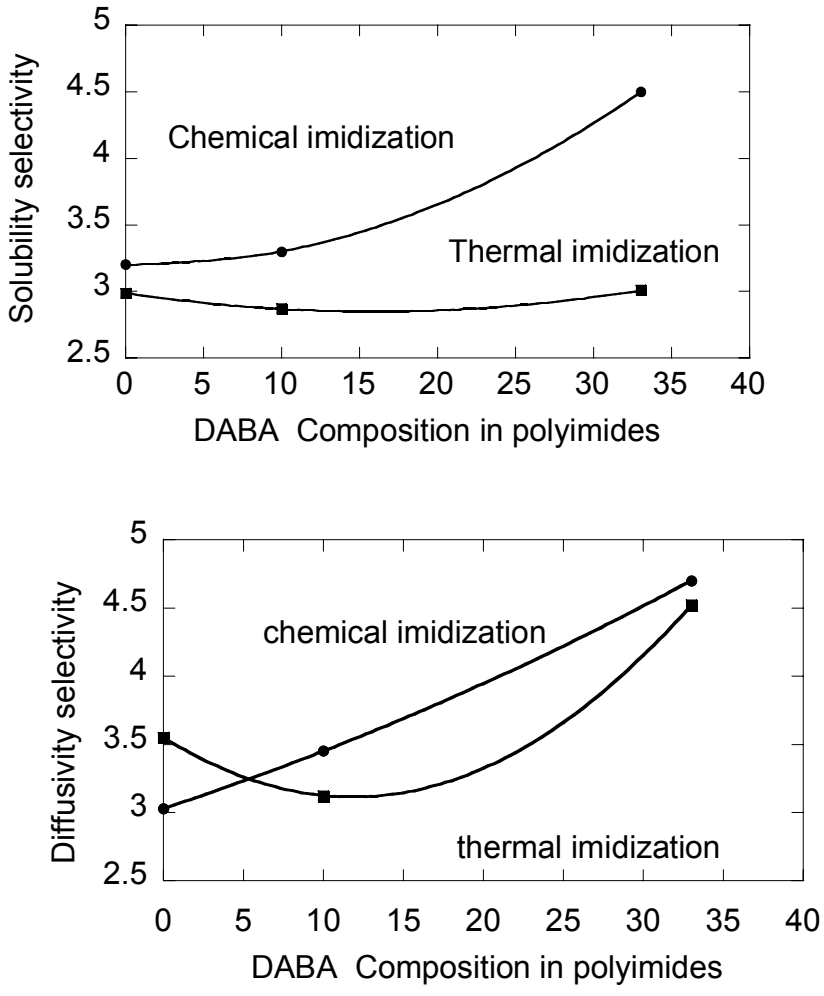
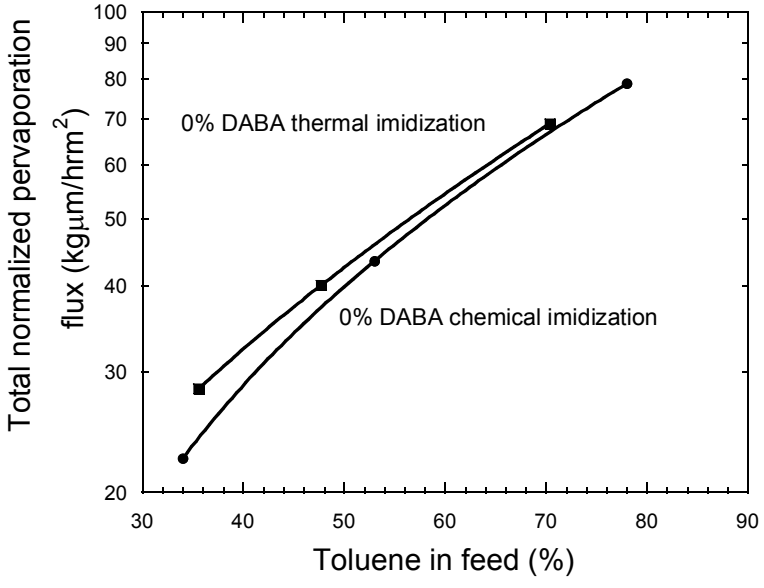


Figure 6.2 Solubility selectivity and diffusivity selectivity of 6FDA-DAM/DABA polyimides in a 50/50 wt% toluene/iso-octane feed at 100°C



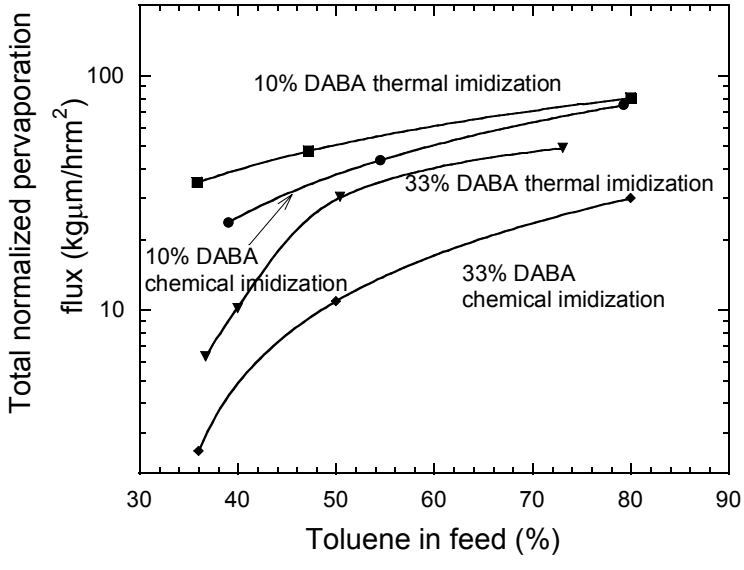
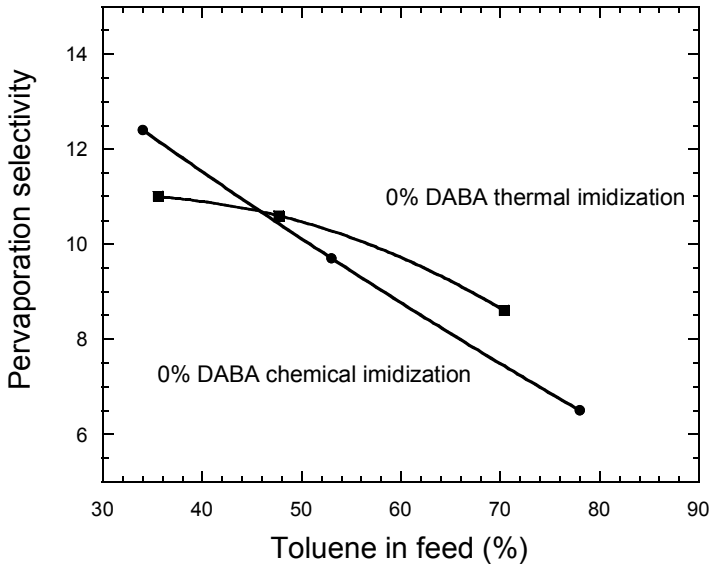


Figure 6.3 Pervaporation performances of membranes made from 6FDA-DAM/DABA polyimides in different toluene/iso-octane feed mixtures



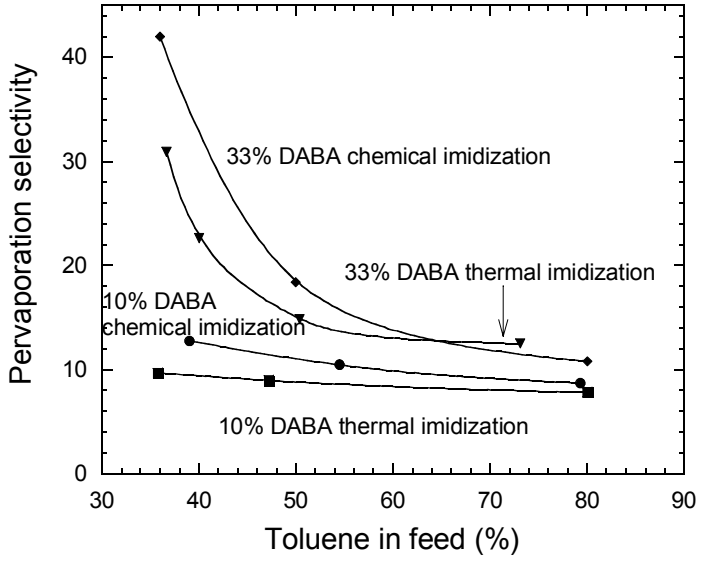
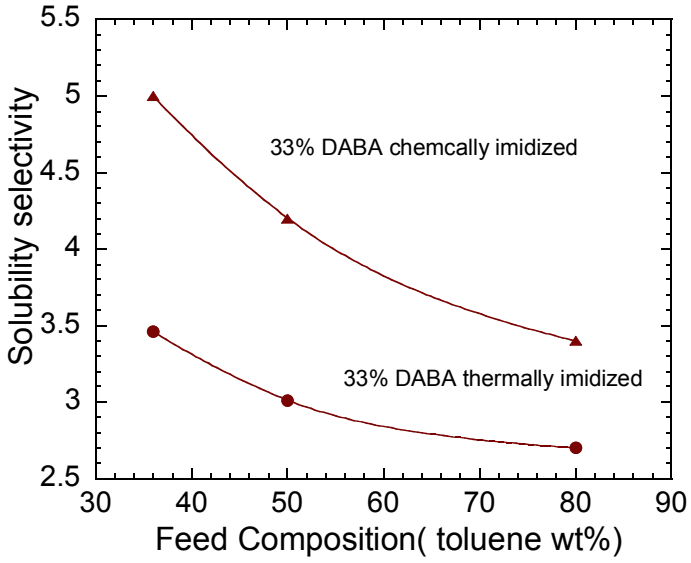


Figure 6.3 Pervaporation performances of membranes made from 6FDA-DAM/DABA polyimides in different toluene/iso-octane feed mixtures, continued

Figure 6.4 shows the solubility and diffusivity characteristics of 6FDA-DAM/DABA(33%) materials for different toluene contents in the feed. The solubility selectivity and diffusivity selectivity of the thermally imidized polyimides decrease more slowly as the toluene concentration in the feed increases than is the case for the chemically imidized polyimides. The solubility selectivity of the thermally imidized materials is lower than that of the chemically imidized materials over the whole range of feed compositions. The diffusivity selectivity of the thermally imidized materials is initially lower than that of the chemically imidized when the toluene concentration in the feed is low. As the toluene concentration in the feed increases beyond 50%, the diffusivity selectivity of the thermally imidized materials shows little change, while the diffusivity selectivity of the chemically imidized materials continue to decrease with toluene content in the feed and is actually lower than that of the thermally imidized materials at high toluene content in the feed.

To illustrate the feed composition effect more clearly, the permeability of 6FDA-DAM/DABA(33%) to toluene and to iso-octane versus feed composition is shown in Figure 6.5. The thermally imidized materials have higher permeability than the corresponding chemically imidized materials. The permeability coefficients of both the chemically imidized and the thermally imidized materials for toluene and iso-octane increase as the toluene concentration increases in the feed. However, the increase of the permeability is less significant for the thermally imidized materials when the toluene concentration in the feed is higher than 50%.



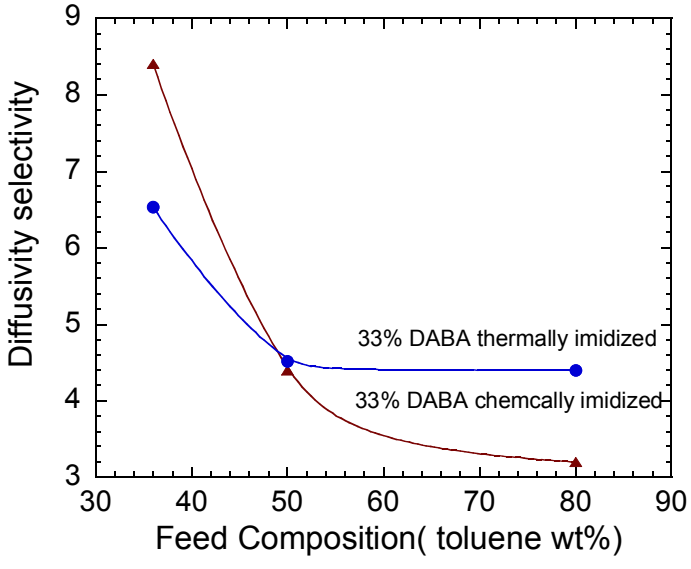


Figure 6.4 Solubility and diffusivity selectivity of 6FDA-DAM/DABA(33%) membranes as a function of the toluene/iso-octane ration in the feed mixtures

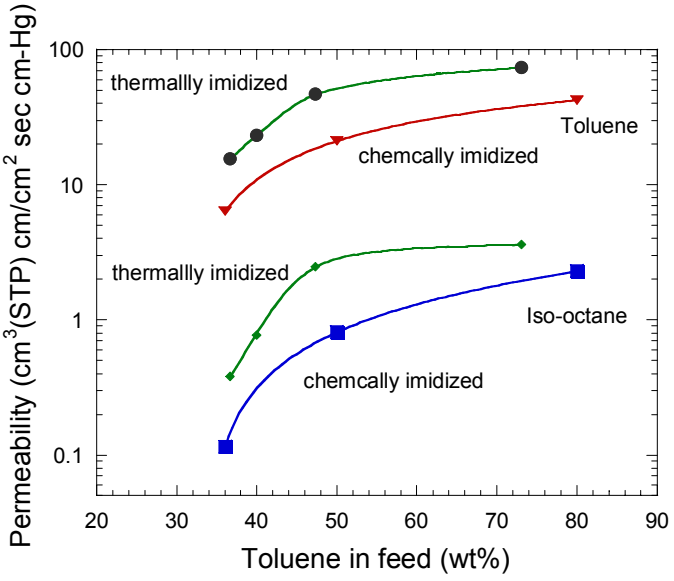


Figure 6.5 Permeability coefficients for 6FDA-DAM/DABA(33%) membranes with different toluene/iso-octane feeds

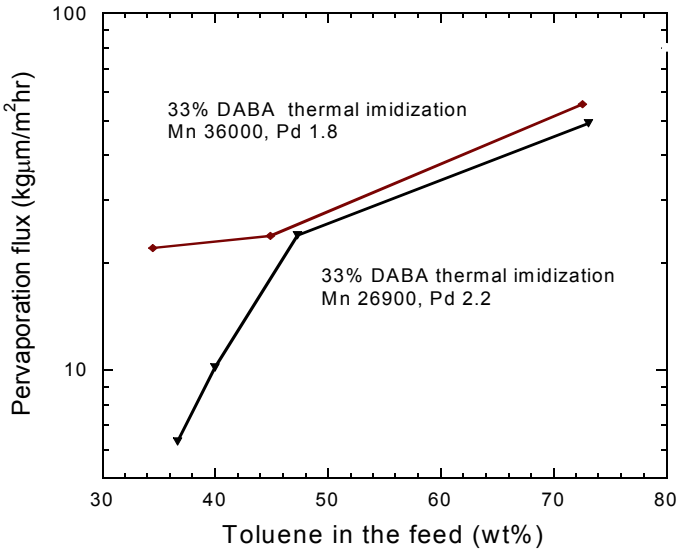
6.1.3 Effect of molecular weight

A few literature references show that molecular weight has some impact on gas permeability [1, 2, 3]. Higher molecular weight polymers tend to have lower film density; thus, higher free volume and higher permeability and lower selectivity for gases, consequently.

The polyimide molecular weight can be controlled by controlling the imidization time in thermal solution imidizaton. However, imidization degree may become an issue resulting from different imidization time. In this study, synthesis of polyimides with different molecular weights was attempted by very carefully controlling the stoichiometry of the

three monomers in the synthesis. Only two batches of 6FDA-DAM/DABA(33%) polyimides were formed to have significantly different molecular weight and to form flexible films for pervaporation tests. The pervaporation performance of these 6FDA-DAM/DABA(33%) polyimides with different molecular weight is shown in Figure 6. 6. The higher molecular weight 6FDA-DAM/DABA(33%) polyimide has higher flux and lower selectivity than the corresponding lower molecular weight polyimide over the whole range of the toluene/iso-octane feeds. When the toluene concentration in the feed is low, the flux and selectivity difference between the two materials is significant; as the toluene concentration in the feed increases, the difference becomes smaller.

The film density of these two 6FDA-DAM/DABA(33%) materials are shown in Table 6.2. The film density of the higher molecular weight material is slightly lower than that of the lower molecular weight material. The lower film density, thus, more free volume, is possibly one of the reasons for the higher molecular weight material having higher free higher flux and lower selectivity in pervaporation. The molecular weight of the thermally imidized 6FDA-DAM/DABA(10%) material discussed in 6.1.1 is 31900, about 20% higher than that of the other materials (molecular weight 24000-27000) in Table 6.1. A 6FDA-DAM/DABA(10%) material with a comparable molecular weight(about 25000) should have lower flux and higher selectivity than that shown in Figure 6.1. This also explains why the thermally imidized 6FDA-DAM/DABA(10%) material shown in Figure 6.1 have slightly higher flux and lower selectivity that the corresponding 6FDA-DAM. If



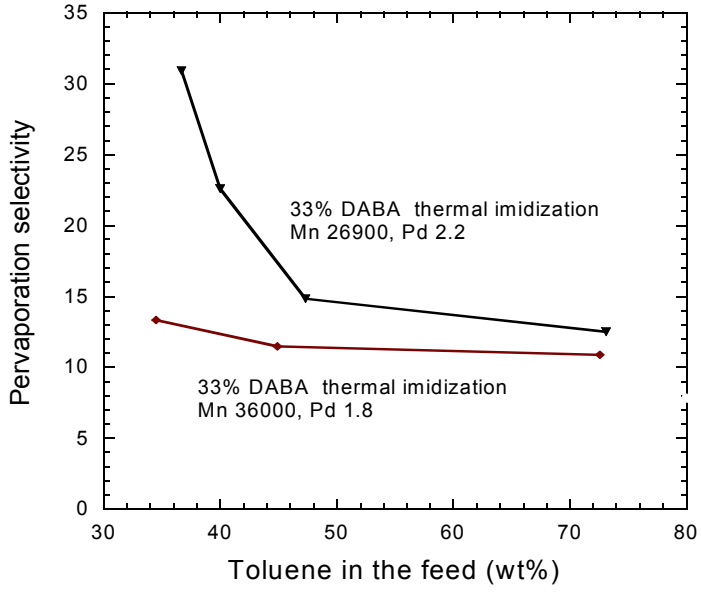


Figure 6.6 Pervaporation performance of 6FDA-DAM/DABA(33%) polyimides with different molecular weights

6FDA-DAM and 6FDA-DAM/DABA(10%) have comparable molecular weight, 6FDA-DAM/DABA(10%) should have lower flux and higher selectivity than 6FDA-DAM.

Table 6.2 Film density of 6FDA-DAM/DABA(33%) membranes having different molecular weights

Molecular weight	36000	26900	Difference
density (g/cm^3)	1.359	1.367	0.008

6.2 Membrane swelling in toluene/iso-octane mixtures

To better understand the effects of DABA content of the polyimide materials and of the toluene concentration in the feed, swelling and sorption tests were conducted. The swelling of a series of 6FDA-DAM/DABA polyimides in pure toluene at 100°C is shown in Figure 6.7. The swelling of the 6FDA-DAM/DABA series materials imidized by the chemical processes decreases as the DABA composition in the polyimide increases. For the thermally imidized 6FDA-DAM/DABA materials, the swelling increases as the DABA composition increases from 0% to 10%, then decreases as the DABA composition increases to 33%. The toluene and iso-octane sorption of 6FDA-DAM/DABA(33%) in the toluene/iso-octane mixtures at 100°C is shown in Figure 6.8. The toluene sorption in the materials imidized by both chemical and thermal processes is very similar. The thermally imidized 6FDA-DAM/DABA(33%) polyimide has significantly higher iso-

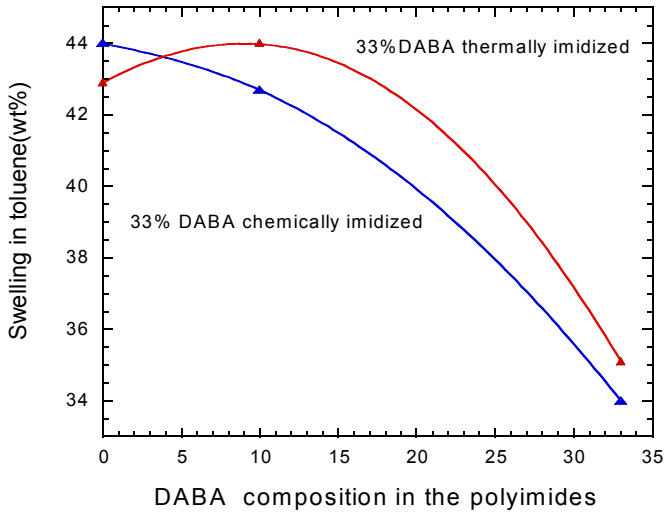


Figure 6.7 Swelling of 6FDA-DAM/DABA polyimides in toluene at 100°C

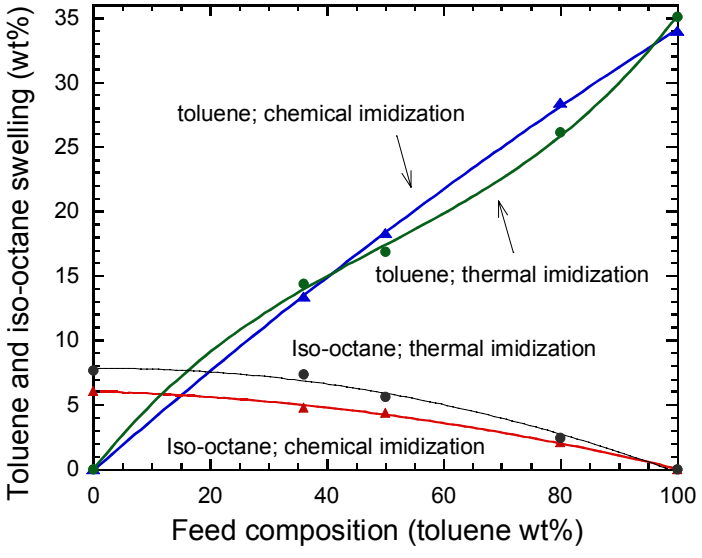


Figure 6.8 Swelling of 6FDA-DAM/DABA(33%) in toluene/iso-octane mixtures at 100°C

octane sorption than the chemical imidized polyimide. The swelling in pure toluene and the sorption results agree with the pervaporation results discussed above.

6.3 Material properties of 6FDA-DAM/DABA polyimides

The transport properties of the 6FDA-DAM/DABA polyimides imidized by chemical and thermal processes are discussed and compared above. To better understand the difference in the transport properties, the material properties of the 6FDA-DAM/DABA series polyimides, such as glass transition temperature, film density and WAXD spectrum were tested. Table 6.3 and Table 6.4 show the glass transition temperature and the film density of the 6FDA-DAM/DABA series polyimides, respectively.

Table 6.3 Glass transition temperature of 6FDA-DAM/DABA series polyimides

DABA composition	Glass transition temperature(°C)		
	Chemical imidization	Thermal imidization	difference
0%	339	321	18
10%	385	372	13
33%	369	356	13

Table 6.4 Film density of the 6FDA-DAM/DABA series polyimdes

DABA composition	density (g/cm^3)		
	chemical imidization	thermal imidization	difference
0%	1.338	1.330	0.008
10%	1.350	1.339	0.011
33%	1.380	1.367	0.013

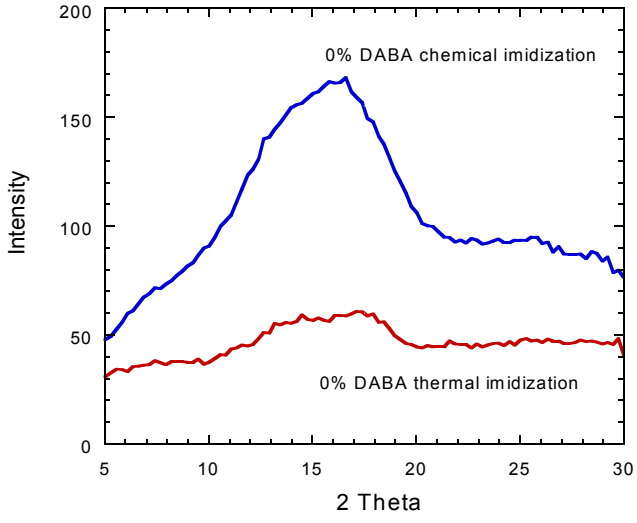


Figure 6.9 WAXD spectra of 6FDA-DAM/DABA series polyimides

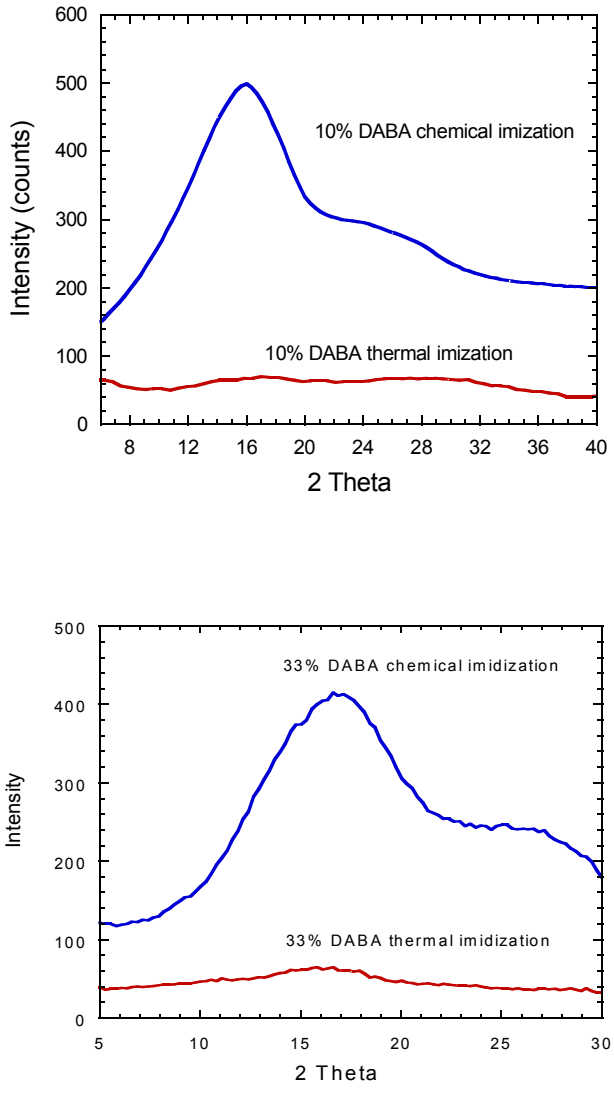


Figure 6.9 WAXD spectra of 6FDA-DAM/DABA series polyimides, continued

The 6FDA-DAM materials synthesized by chemical and thermal imidization have similar film densities. For the polyimides containing DABA groups, chemical imidization produces films with higher film density and glass transition temperature than does

thermal imidization. Figure 6.9 is the WAXD spectra of 6FDA-DAM/DABA series polyimides. The 6FDA-DAM/DABA polyimides imidized by chemical and thermal imidization processes are amorphous materials. However, the chemically imidized polyimides have broad peaks around 8°, indicating a 5.6 Å d-spacing. The glass transition temperature, the film density and the WAXD spectra results imply that the chemically imidized polyimides have better chain packing than the thermally imidized polyimdes. The chemically imidized polyimides with better chain packing show higher selectivity and lower flux in the pervaporation than the thermally imidized polyimides do.

Chemical and thermal imidization produce the 6FDA-DAM/DABA polyimides with different chain packing. The reason for the different chain packing may result from several factors, such as thermal history, film cast process, etc. In this study, the synthesized poyimides were solution-cast using the same procedure. The thermal history during the synthesis process is eliminated by using the same solution casting procedure. The different chain packing likely stems from the differences in chemical structure, and will be discussed in Chapter 7.

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Chapter 7 Chemical structure of 6FDA-DAM/DABA polyimides

The transport and material properties of 6FDA-DAM/DABA polyimides synthesized by chemical imidization and thermal imidization are discussed in Chapter 5 and Chapter 6, respectively. The difference of the transport and material properties between chemically imidized polyimides and thermally imidized polyimides may be the result of difference in the structure of the polymers produced by the two imidization processes. In this chapter, the chemical structures of the polyimides discussed in Chapter 5 and Chapter 6 are probed by UV-VISIBLE, FTIR and NMR spectroscopy, and will be compared.

7.1 UV-VISIBLE spectrum

It was mentioned in Chapter 2 that chemical imidization may lead to a high percentage of isoimide in the imidization product. The isoimide can be detected by UV-VISIBLE spectroscopy. Figure 7.1 is a typical UV-VISIBLE spectrum of imide and isoimide [1]. Imide has a strong peak at 289nm, and isoimide has a broad peak at 385 nm. Figure 7.2 shows the full spectrum of the 6FDA-DAM/DABA polyimides synthesized by chemical imidization. The strong peaks at 293 nm are imide peaks. Figure 7.3 is the spectra for the 6FDA-DAM/DABA polyimides synthesized by thermal method. The UV-visible spectra of 6FDA-DAM/DABA polyimides synthesized by chemical and thermal methods are very similar. No significant isoimide peaks are observed for chemical imidized polyimides in Figure 7.2. The UV-visible spectra show that the chemical imidized 6FDA-DAM/DABA polymer materials in this study do not contain isoimides, which agrees with

the argument that when triethylamine is used as the catalyst, the chemical imidization process does NOT produce isoimides [2].

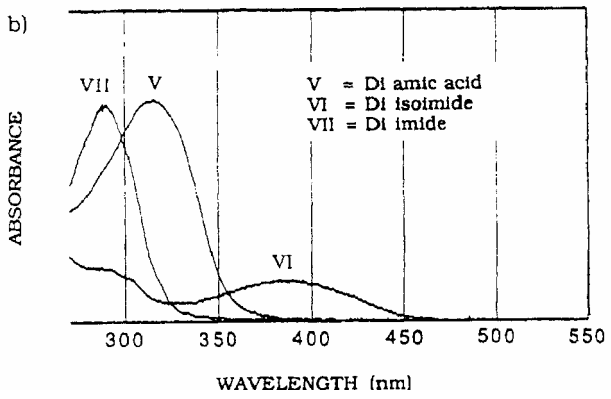


Figure 7.1 Typical UV-visible spectrum of imide and isoimide

Source: J.W. Park, etc. Macromolecules, 27(1994), 3459-3463

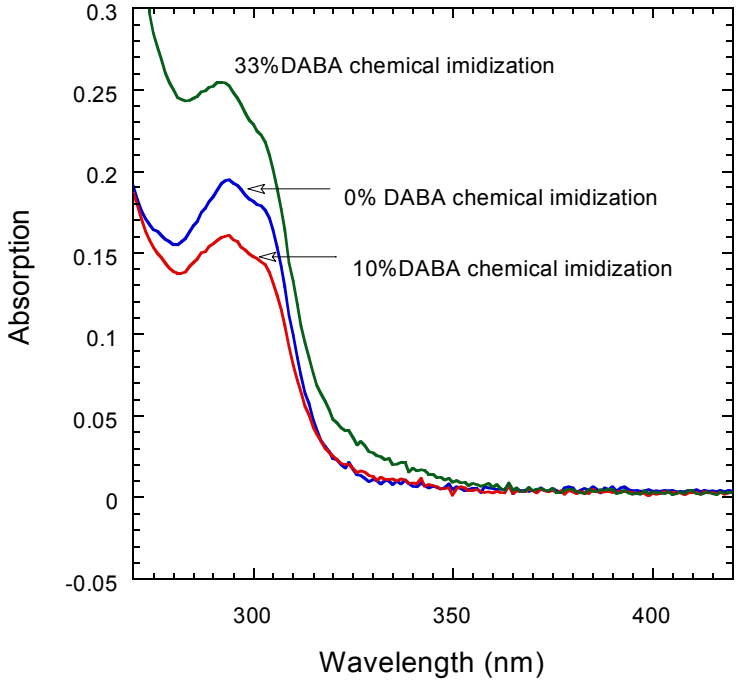


Figure 7.2 Full UV-visible spectrum of chemical imidized 6FDA-DAM/DABA polyimides

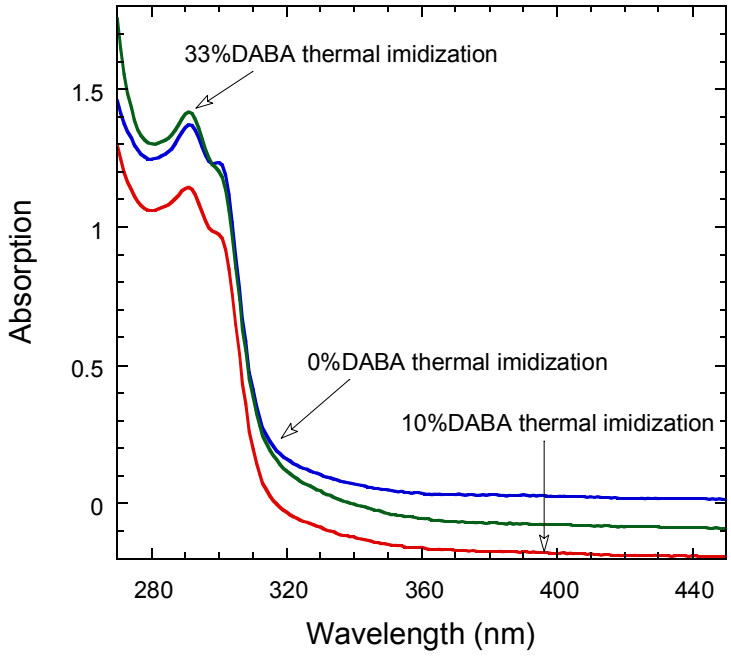


Figure 7.3 UV-visible spectra of thermal imidized 6FDA-DAM/DABA polyimides

7.2 FTIR spectrum

The chemical structure of 6FDA-DAM/DABA polyimides could be characterized by FTIR spectroscopy. The characteristic imide and amic acid absorption bands are shown in Table 7.1 [3]. Figure 7.4 is the FTIR spectra of 6FDA-DAM/DABA polyimides. For the 6FDA-DAM and 6FDA-DAM/DABA (10%) materials, chemical imidized and thermal imidized materials have very similar spectra, and do NOT show any amic acid characteristic peaks. For the 6FDA-DAM/DABA(33%) materials, no amic acid characteristic peaks are observed for the thermal imidized polyimide, while the chemical imidized polyimide has small amic acid peaks at 1550cm^{-1} (C-NH) and 1650cm^{-1}

(C=ONH). The chemical imidization of 6FDA-DAM/DABA (33%) polyimide is not complete. However, its imidization degree cannot be quantified due to the quantitative limitation of FTIR spectroscopy.

Table 7.1 Characteristic imide and amic acid absorption bands

	Absorption band	Intensity	Origin
aromatic	1780	Strong	C=O asym. stretch
imides	1720	Very strong	C=O sym stretch
	1380	Strong	C-N stretch
	725	weak	C=O bending
amic	2900-3200	Medium	COOH and NH
acids	1710	Strong	C=O(COOH)
	1660	Strong	C=O(CONH)
	1550	medium	C-NH

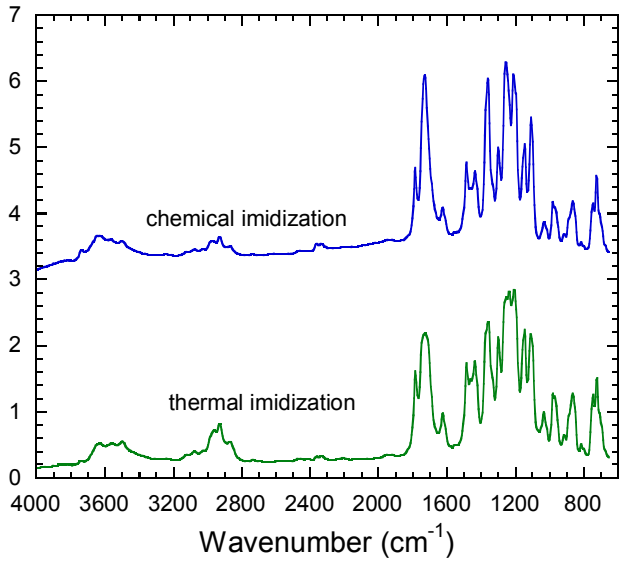


Figure 7.4(a) FTIR spectrum of 6FDA-DAM polyimides

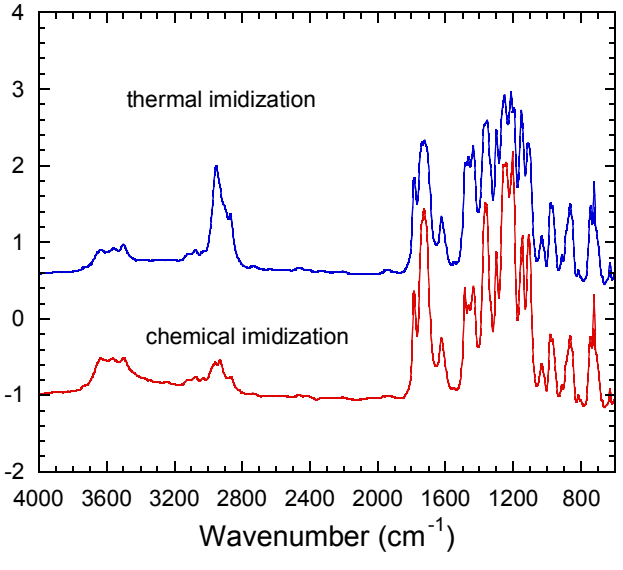


Figure 7.4 (b) FTIR spectrum of 6FDA-DAM/DABA (10%) polyimides

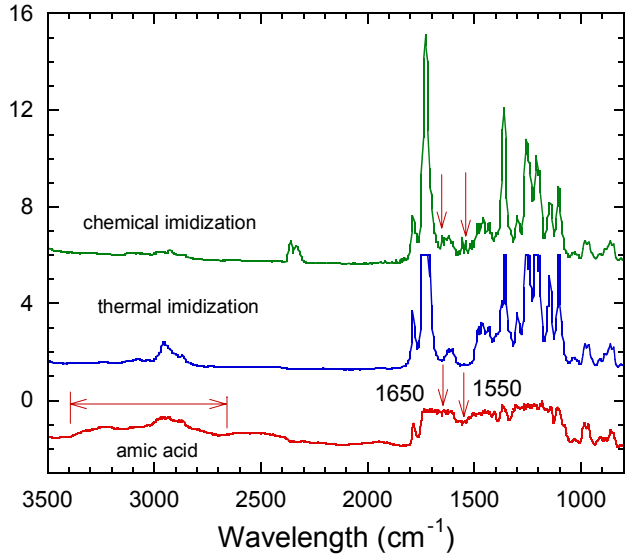


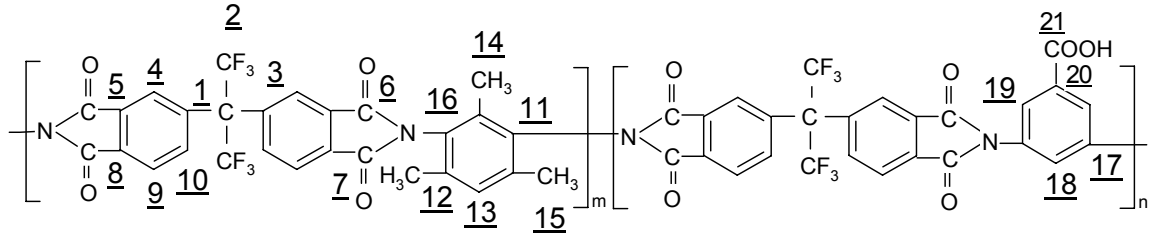
Figure 7.4 (c) FTIR spectrum of 6FDA-DAM/DABA (33%) polyimides and polyamic acid

7.3 NMR

7.3.1 ^{1}H NMR

NMR is an excellent characterization tool for quantifying polymer structure and composition. ^{1}H NMR has the advantage of speedand high sensitivity because of the abundance of ^{1}H in polymers. Figure 7.5 is the ^{1}H NMR spectra of 6FDA-DAM/DABA polyimides. The characteristic imide peaks (H4, H9 and H10) have chemical shifts around 8 ppm, and carboxylic acid either has a very broad peak above 9 ppm, or doesn't show any peaks. If the imidization is not complete, an amid peak occur around 10 ppm[4]. The peaks between 7.90-7.98ppm, which increase as DABA composition increases, belong to H19 and H18 of diamine DABA. The two peaks around 2ppm are

H15 and H14 of diamine DAM. The peak sequence of H4, H9 and H10 in Figure 7.7(C) is determined with the assistance of C-H correlation spectrum in Figure 7.9, which will be discussed later.



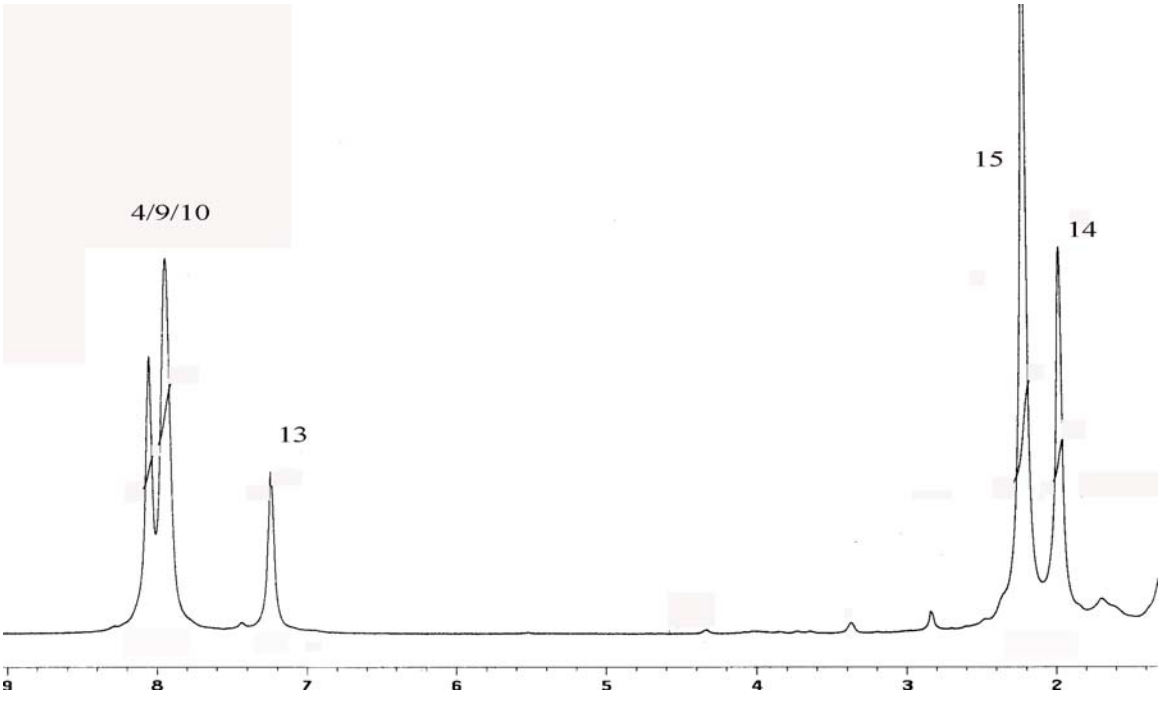


Figure 7.5(a) ^{1}H NMR spectra of 6FDA-DAM polyimides.

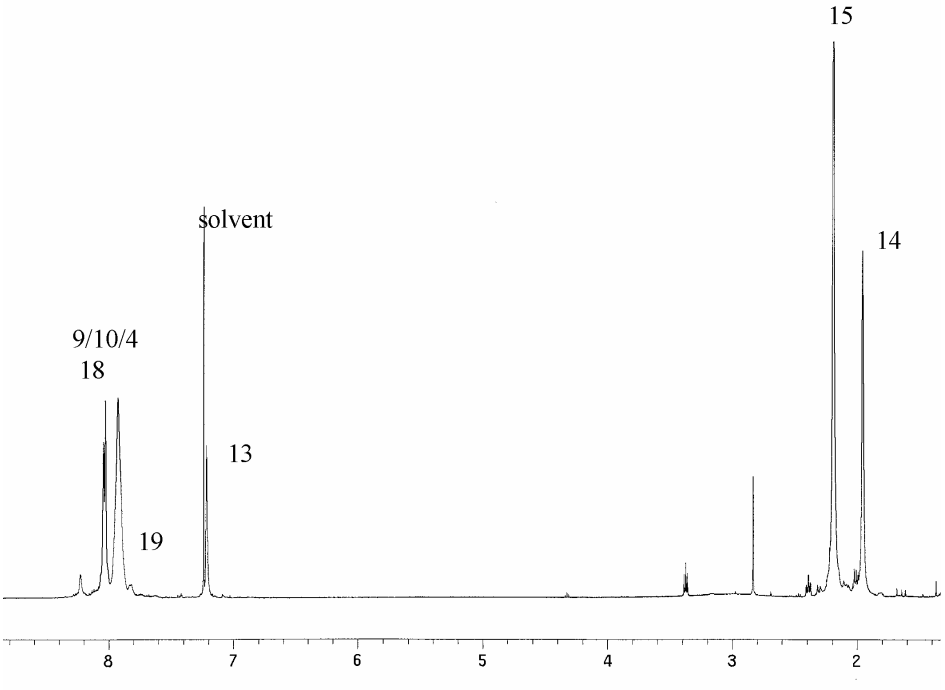


Figure 7.5(b) ^{1}H NMR spectra of 6FDA-DAM/DABA(10%) polyimides.

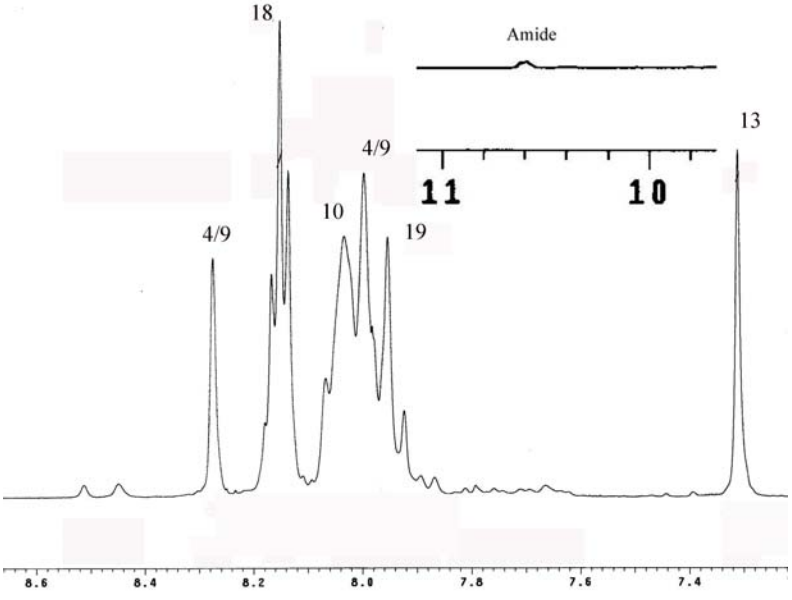


Figure 7.5(c) ^{1}H NMR spectra of 6FDA-DAM/DABA(33%) polyimides

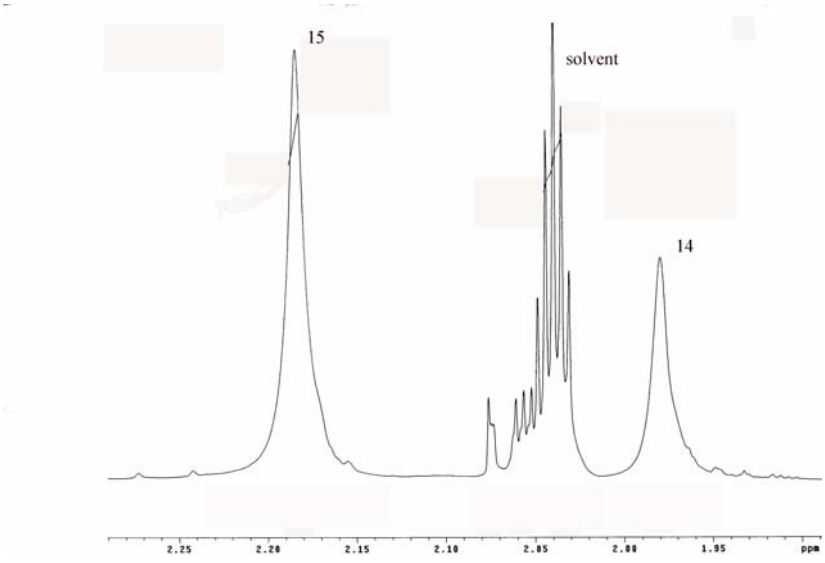


Figure 7.5 ^{1}H NMR spectra of 6FDA-DAM/DABA(33%) polyimides, continued

7.3.1.1 Copolymer composition

In this study the composition of 6FDA-DAM/DABA co-polyimides are controlled by adding stoichiometric amounts of monomers and assuming all the monomers are reacted into polymer during the synthesis. The composition of the co-polyimide is verified by the ^{1}H NMR spectrum. Table 7.2 shows the composition of 6FDA-DAM/DABA(10%) and 6FDA-DAM/DABA(33%) polyimides calculated by the peak area ratio of H14 and H15 vs. H4, H9 and H10.

For 6FDA-DAM material in Figure 7.5(a), the characteristic imide peaks (H4, H9 and H10) are two simple close peaks, while for 6FDA-DAM/DABA(33%) material in Figure 7.5(C), these characteristic peaks are split into two groups of peaks. The peak splitting is

due to the H-H coupling affected by the two different diamines connected to the dianhydride.

7.3.1.2 Imidization degree

The 6FDA-DAM and 6FDA-DAM/DABA(10%) polyimides in Figure 7.5(a) and Figure 7.5(b) do not show any signals above 8.2ppm. However, the 6FDA-DAM/DABA(33%) poyimides imidized by chemical and thermal methods both have a weak amic acid peak at 10.6ppm. The amount of the amic acid cannot be quantified because the solvent contains a comparable amount of water (a very broad peak at 3.4ppm), and the protons in the water and in the amic acid are interchangeable in the NMR spectrum.

Table 7.2 Composition of 6FDA-DAM/DABA co-polyimdes calculated from ^{1}H NMR

	Chemical imidized	Thermal imidized
10% DABA	11%	10%
33% DABA	34%	31%

7.3.2 ^{13}C NMR

To avoid the inference of the water, ^{13}C NMR is used to quantify the degree of imidization for 6FDA-DAM/DABA(33%) polyimides. Figure 7.6 and Figure 7.7 are the ^{13}C NMR spectra of three monomers used in this study. Figure 7.8 and Figure 7.10 show the DEPT45 NMR spectrum and C-H correlated spectrum of 6FDA-DAM/DABA(33%),

respectively. The DEPT45 (Distortionless Enhancement by Polarization Transfer) spectrum observes protonated carbons only, which are C4, C9, C10, C13, C18 and C19 in Figure 7.8. Figure 7.9 is the C-H correlation NMR spectrum of 6FDA-DABA. With the aid of C-H correlation spectra in Figure 7.9 and Figure 10, the peaks in Figure 7.8 are assigned. The spectra of monomer DAM and DABA are assigned according to the spectra from the NMR database[5], then the 6FDA-DAM and 6FDA-DAM/DABA(33%) spectra in Figure 7.7 are assigned. The characteristic imide peaks C6 and C7, and carboxylic acid have chemical shift around 166 ppm. If the imidization is not complete, the amide has a peak above 170 ppm.

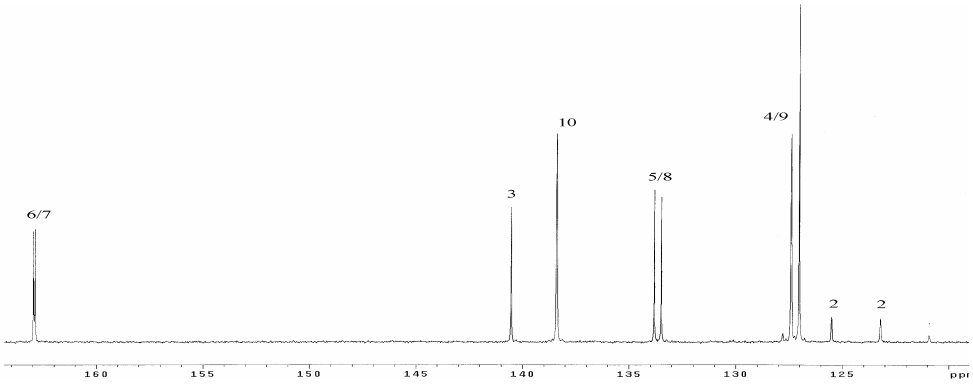


Figure 7.6(a) ^{13}C NMR spectrum of 6FDA monomer used in this study

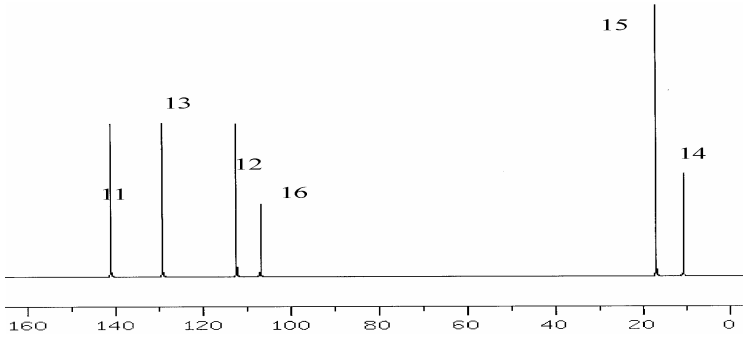


Figure 7.6(b) ^{13}C NMR spectrum of DAM monomer used in this study
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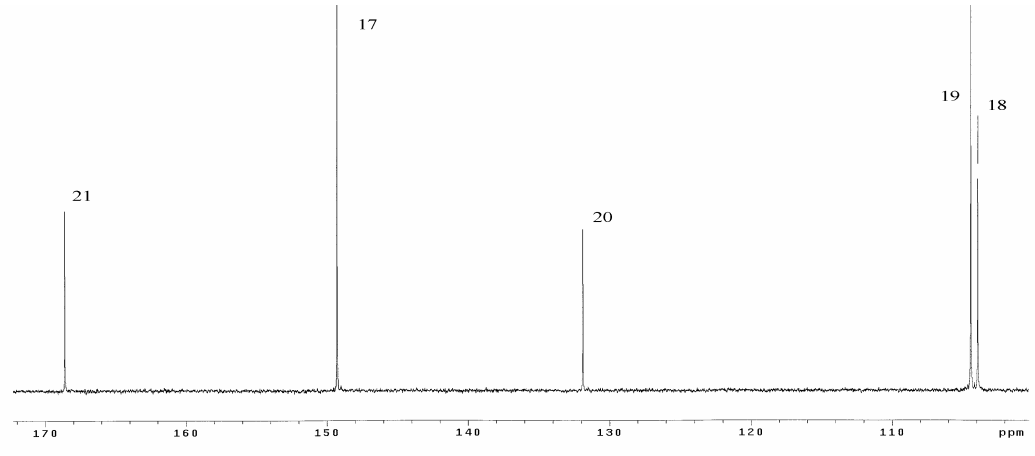


Figure 7.6(c) ^{13}C NMR spectrum of DABA monomer used in this study

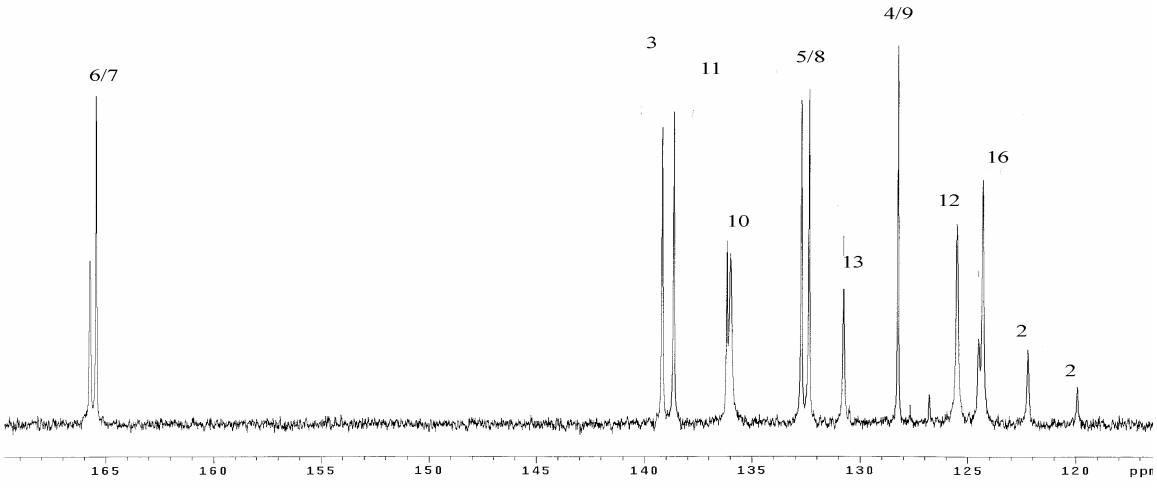


Figure 7.7(a) ^{13}C NMR spectrum of 6FDA-DAM

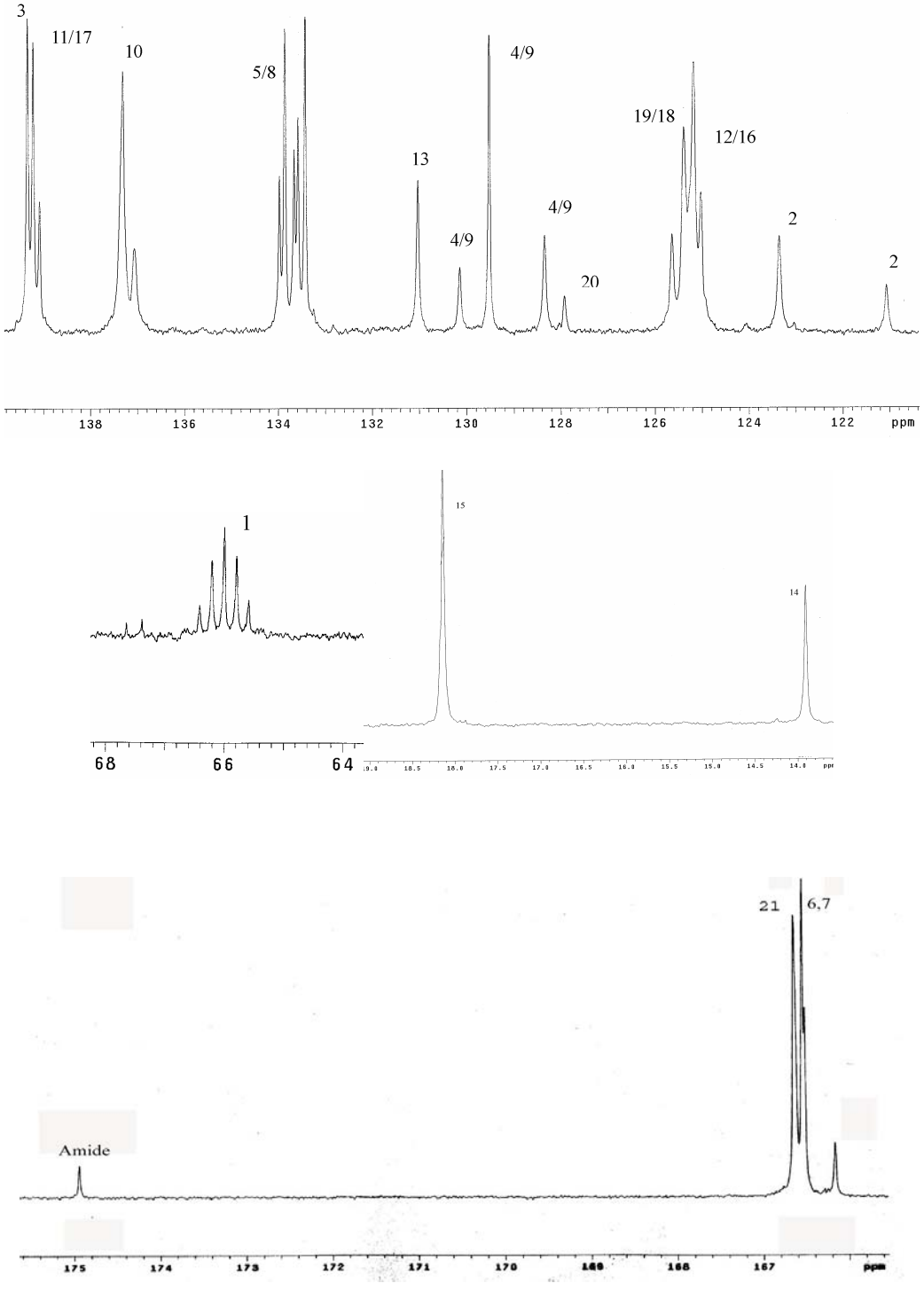


Figure 7.7(b) ^{13}C NMR spectra of 6FDA-DAM/DABA(33%)

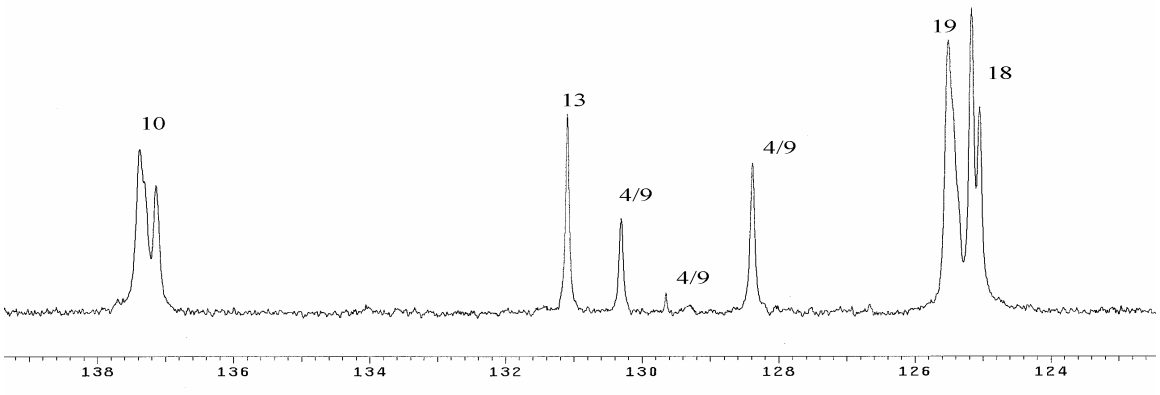


Figure 7.8 DEPT spectrum of 6FDA-DAM/DABA(33%)

The 6FDA-DAM/DABA(33%) polyimides imidized by chemical and thermal methods both have a weak amide peak at 174.9 ppm. The percentage of the amic acid can be calculated by the peak area ratio of amide acid vs. C14 and C15. Table 7.3 shows the calculated imidization degree of 6FDA-DAM/DABA(33%) polyimides.

The thermal imidization procedure led to a higher degree of imidization than the chemical imidization for the 6FDA-DAM/DABA(33%) materials. For the 6FDA-DAM/DABA(10%) materials, the NMR spectra show 100% imidization. However, considering the sensitivity of NMR, it is possible that there is small difference of imidization degree between the chemical imization and the thermal imidization. The different imidization degree means a different chemical structure. The chemically imidized materials contain more carboxylic acid than the thermally imidized one, and

have better chain packing consequently, which agrees with the material and transport properties discussed in Chapter 5 and Chapter 6.

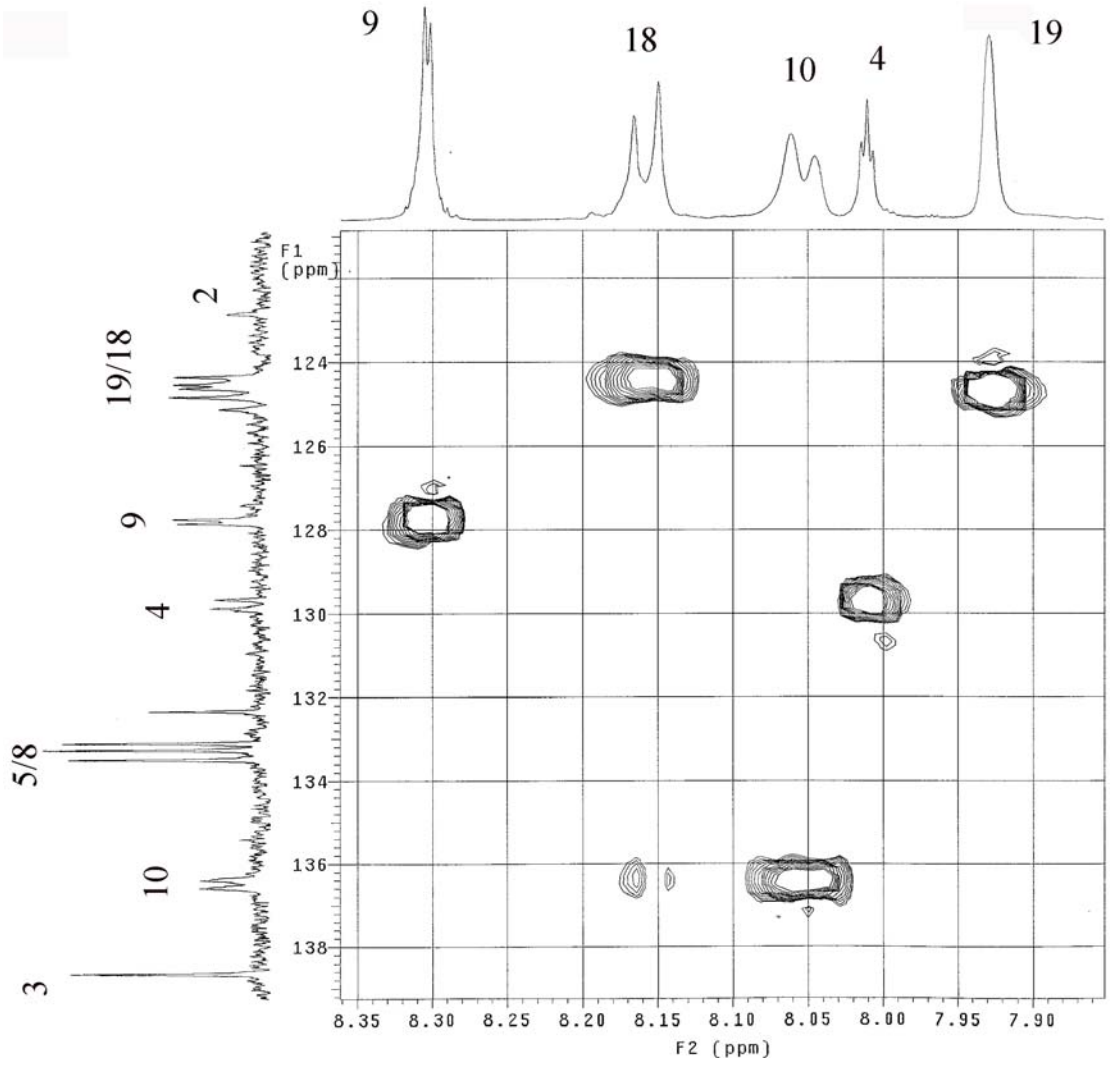


Figure 7.9 C-H correlation NMR spectrum of 6FDA-DABA

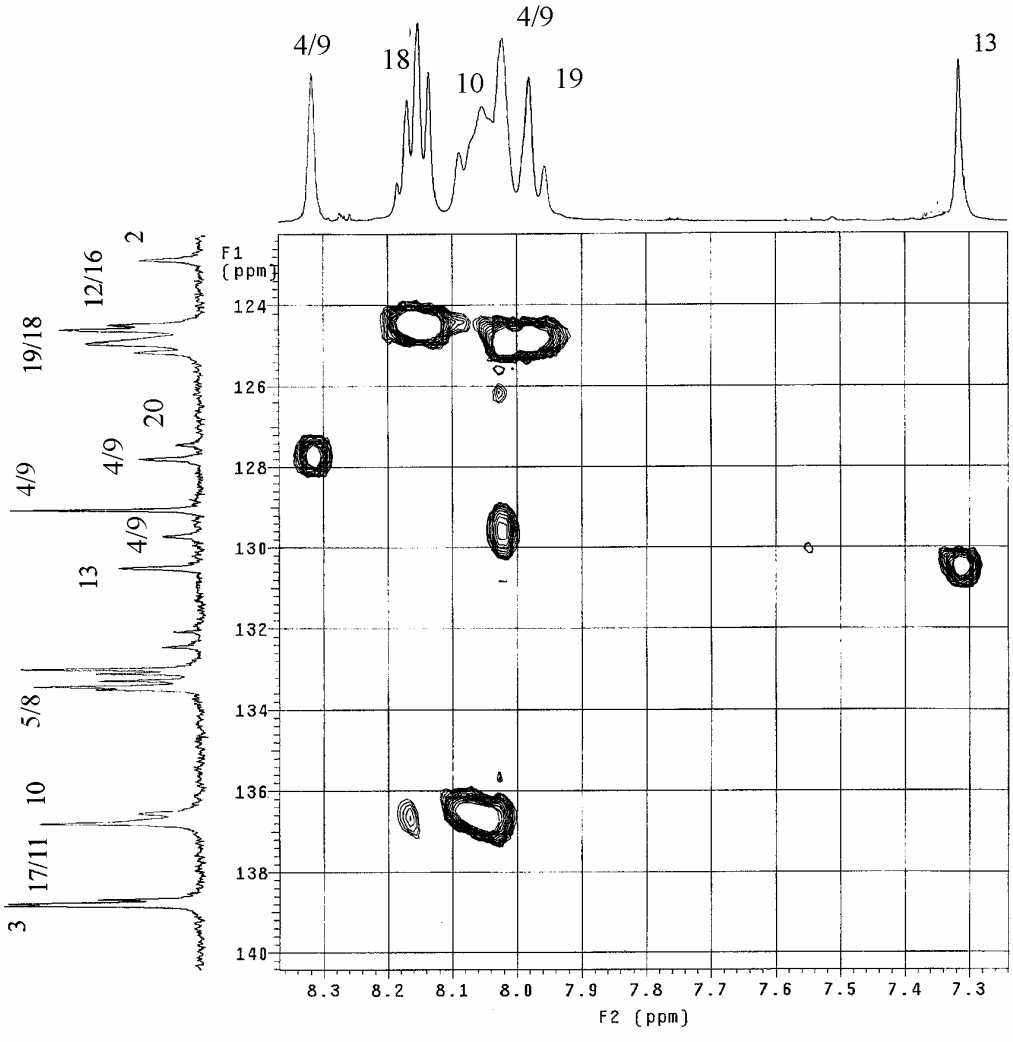


Figure 7.10 C-H correlation spectrum of 6FDA-DAM/DABA(33%)

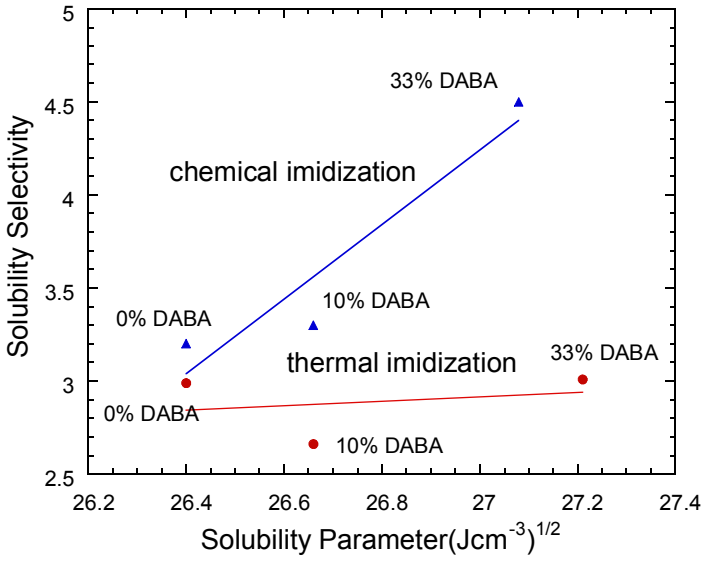
Table 7.3 Imidization degree of 6FDA-DAM/DABA(33%) polyimides

	Chemically imidized	Thermally imidized
Percentage of amic acid	15%	4%
Imidization degree	85%	96%

The imidization process may be related to the concentration of DABA in the polymer. The higher DABA concentration, the more difficult the imidization is. Thermal imidization is more suitable for higher DABA concentration imidization than chemical imidization.

7.4 Structure-transport correlations

In Chapter 5 the solubility selectivity and diffusivity selectivity of the chemically imidized 6FDA-DAM/DABA membranes were correlated with their solubility parameters and inverse fractional free volume, respectively. Because of the incomplete imidization in 6FDA-DAM/DABA(33%) membranes, the solubility parameter and fractional free volume of the 6FDA-DAM/DABA(33%) are recalculated, and the correlations for the chemically imidized and the thermally imidized membranes are shown in Figure 7.11. For membranes with same solubility parameter, the chemically imidized membranes have significantly higher solubility selectivity than the thermally imidized membranes. However, for membranes with same fractional free volume, the chemical imidized membranes have significantly lower diffusivity selectivity than the thermally imidized membranes. The correlations show that though the incomplete imidization issue is considered, the structure-transport relations of the chemically imidized membranes and the thermally imidized membranes are still different. This implies that the impacts of imidization method in polyimide structure and properties are complicated and not limited to the imidization degree. These impacts should be studied more fully.



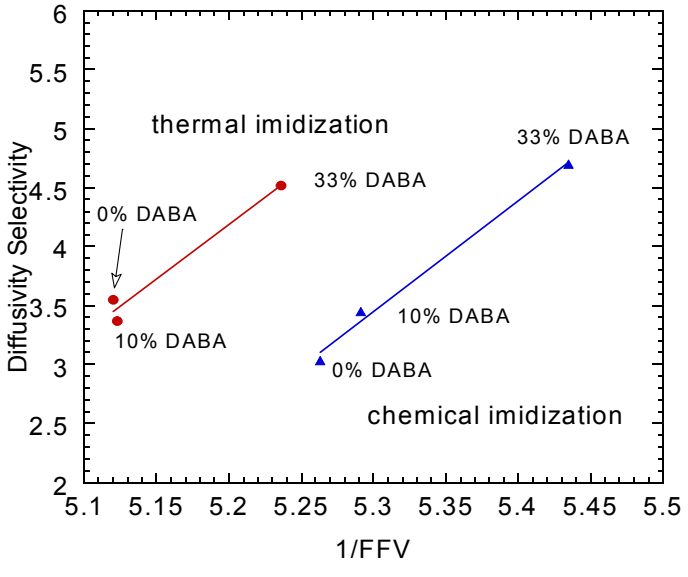


Figure 7.11 Structure-transport correlations for 6FDA-DAM/DABA polyimides

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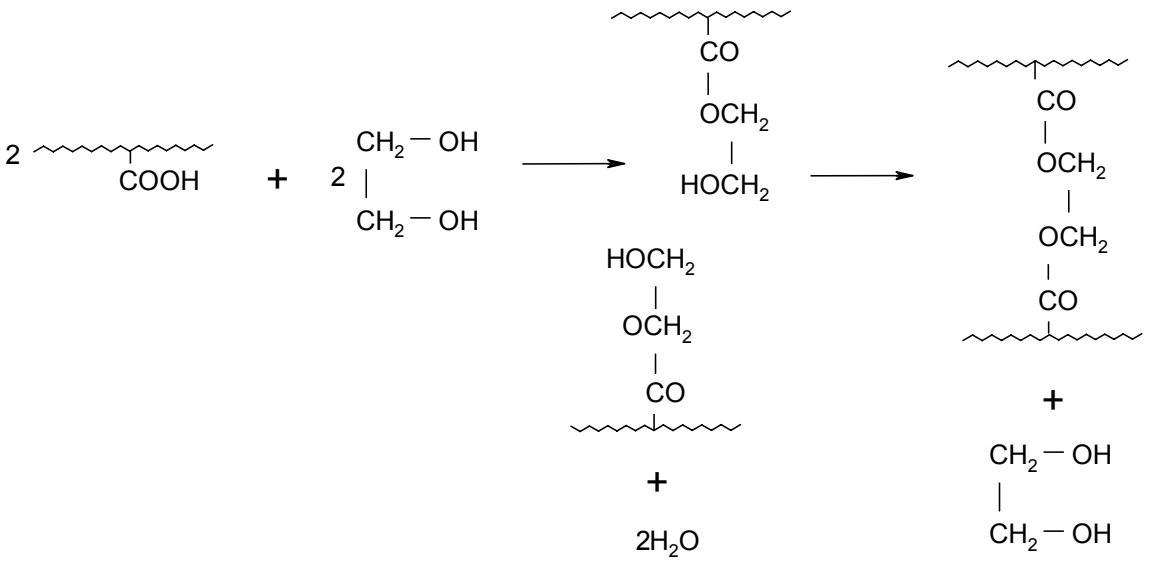
Chapter 8 Covalent crosslinking of 6FDA-DAM/DABA polyimides

In previous chapters, the chemical structure, material and transport properties of 6FDA-DAM/DABA polyimdes, synthesized by chemical imidization and thermal solution imidization, were discussed. The purpose of introducing DABA groups into the polyimide structure is to facilitate chain packing, and to reduce the swelling caused by toluene, which should reduce the plasticization and improve pervaporation performance. The transport results show that the pervaporation selectivity increases significantly with the addition of DABA. However, the membrane plasticization is not effectively reduced.

Crosslinking is an effective approach to reduce plasticization of membranes and improve pervaporation performance. It is believed that appropriate crosslinking can break the performance trade-off by giving a significant increase in selectivity without a large sacrifice of flux. In this chapter, 6FDA-DAM/DABA polyimdes, synthesized by chemical imidization and thermal imidization, are crosslinked by ethylene glycol with the procedure described in Chapter 3. The crosslinking mechanism is shown in Scheme 8.1. It is a two-step crosslinking process, involving mono-esterification in solution and an ester-exchange reaction by heating a solid state membrane to complete crosslinking. This crosslinking method produces defect-free dense membranes and may permit hollow fiber and composite membrane formation. The transport and material properties of the crosslinking membranes are tested and compared with the control materials.



Scheme 8.1 Mechanism of 6FDA-DAM/DABA polyimides crosslinked by ethylene glycol

8.1 Crosslinking of chemically imidized 6FDA-DAM/DABA polyimides

The chemically imidized 6FDA-DAM/DABA(10%) and 6FDA-DAM/DABA(33%) were crosslinked by ethylene glycol. The crosslinked 6FDA-DAM/DABA(33%) polyimides are too brittle to endure pervaporation tests. The 6FDA-DAM/DABA(10%) polyimides form flexible membranes with adequate mechanical properties to allow pervaporatrion testing after crosslinking. The pervaporation performance of the 6FDA-DAM/DABA(10%) polyimides crosslinked by ethylene glycol with various heating times was tested with results shown in Figure 8.1. The separate points at zero heating time for each feed in Figure 8.1 refer to the original 6FDA-DAM/DABA(10%) materials, and the fitted points at zero heating time refer to mono-ester membranes. The mono-ester

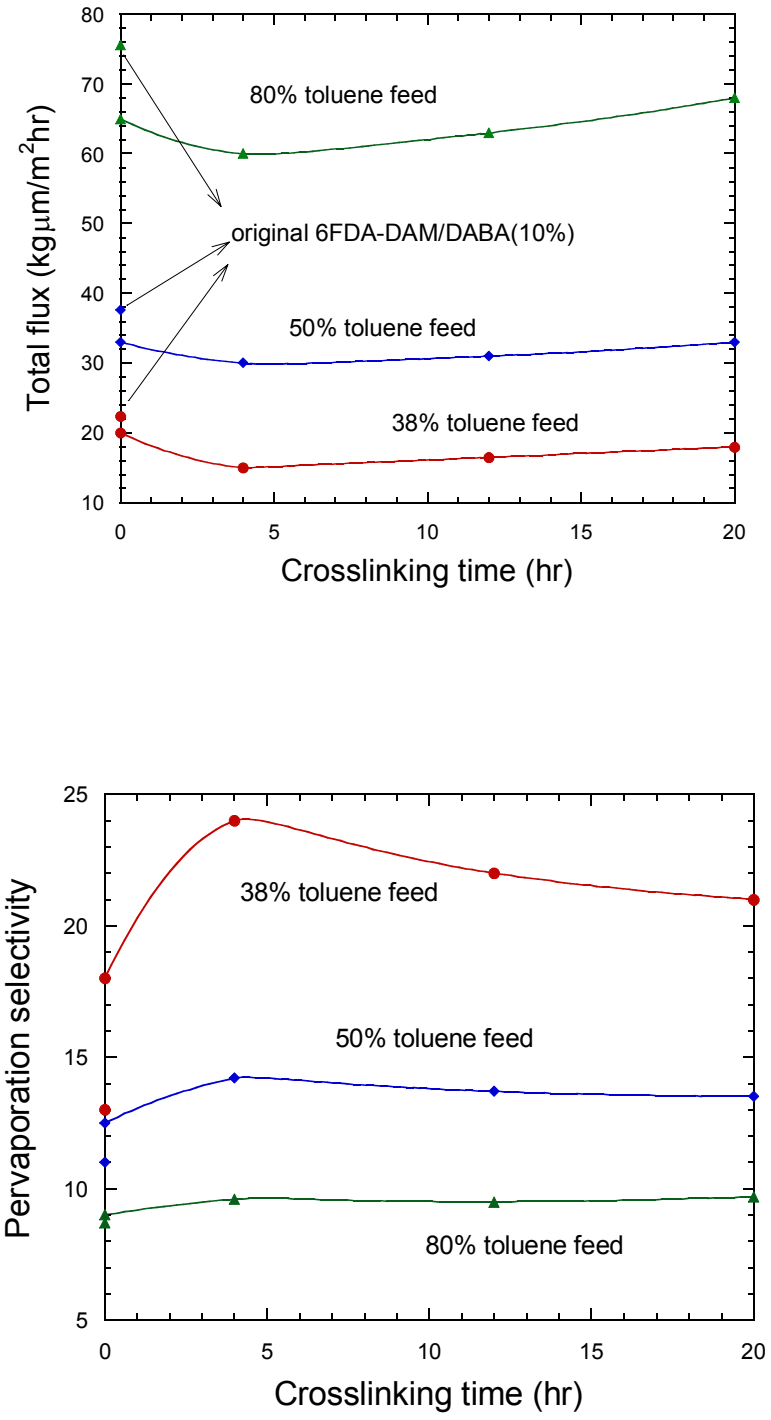


Figure 8.1 Pervaporation performance of chemically imidized 6FDA-DAM/DABA(10%)

membranes have higher pervaporation selectivity and lower flux than the original polyimides. For the 38% and 50% toluene feed, membranes after 4-hours of heating have the highest selectivity, the selectivity decreases slightly as the heating time increases. For the 80% toluene feed, the selectivity continues to increases slowly as the heating time increases. The crosslinking by ethylene glycol is almost finished when the mono-ester membranes are heated for 4 hours. Extending heating time does not change the pervaporation selectivity and flux significantly.

For the 80% toluene feed, the crosslinking does not improve the pervaporation selectivity of 6FDA-DAM/DABA(10%) significantly compared to the original polyimide. The mechanical properties of the crosslinked 6FDA-DAM/DABA(10%) chemically imidized membranes were poor after the pevaporation tests; the membranes were wrinkled and slightly brittle. The ethylene glycol crosslinking for chemically imidized 6FDA-DAM/DADABA(10%) was not successful.

8.2 Crosslinking of thermally imidized 6FDA-DAM/DABA polyimides

Thermally imidized 6FDA-DAM/DABA(10%) and 6FDA-DAM/DABA(33%) polyimides are crosslinked with ethylene glycol. Only the 6FDA-DAM/DABA(10%) polyimides form flexible membranes after crosslinking. The pervaporation performance of the crosslinked 6FDA-DAM/DABA(10%) is shown in Figure 8.2. The separate points at zero heating time in Figure 8.2 refer to the original 6FDA-DAM/DABA(10%) polyimides, and the fitted points at zero heating-time are mono-ester membranes. The

monoester membranes have higher pervaporation selectivity and lower flux than the original membranes. The membranes with 4-hour heating time have the lowest pervaporation flux, and the flux increases slowly as the heating time increases. For the 35% toluene feed, membranes with 9-hour heating have the highest pervaporation selectivity; for the 50% toluene feed and the 70% toluene feed, membranes with 4-hour heating have the highest pervaporation selectivity, then, the selectivity decreases slowly as the heating time increases. The film density of crosslinked 6FDA-DAM/DABA(10%) with different crosslinking time is also shown in Figure 8.2. The membranes heated for 4 hours have the highest film density, which agrees with its pervaporation performance. Membranes with other crosslinking time have similar film density around 1.340 g/cm^3.

The pervaporation performance shows that the optimal crosslinking time for ethylene glycol crosslinking is 4 hours for the thermally imidized 6FDA/DAM/DABA(10%). Increasing crosslinking time slightly increases pervaporation flux, and decreases selectivity at the same time.

8.3 Impact of the crosslinking process on the 6FDA-DAM/DABA polyimide

This polyimide membrane crosslinking process involves a high temperature treatment at 220°C which imposes a significant 'annealing effect' in addition of any crosslinking for most of the polymeric membranes. High temperature will also facilitate charge transfer complex formation that inherently exists in some polyimide membranes. Polymers that are able to undergo charge transfer complex formation consist of two types of monomers:

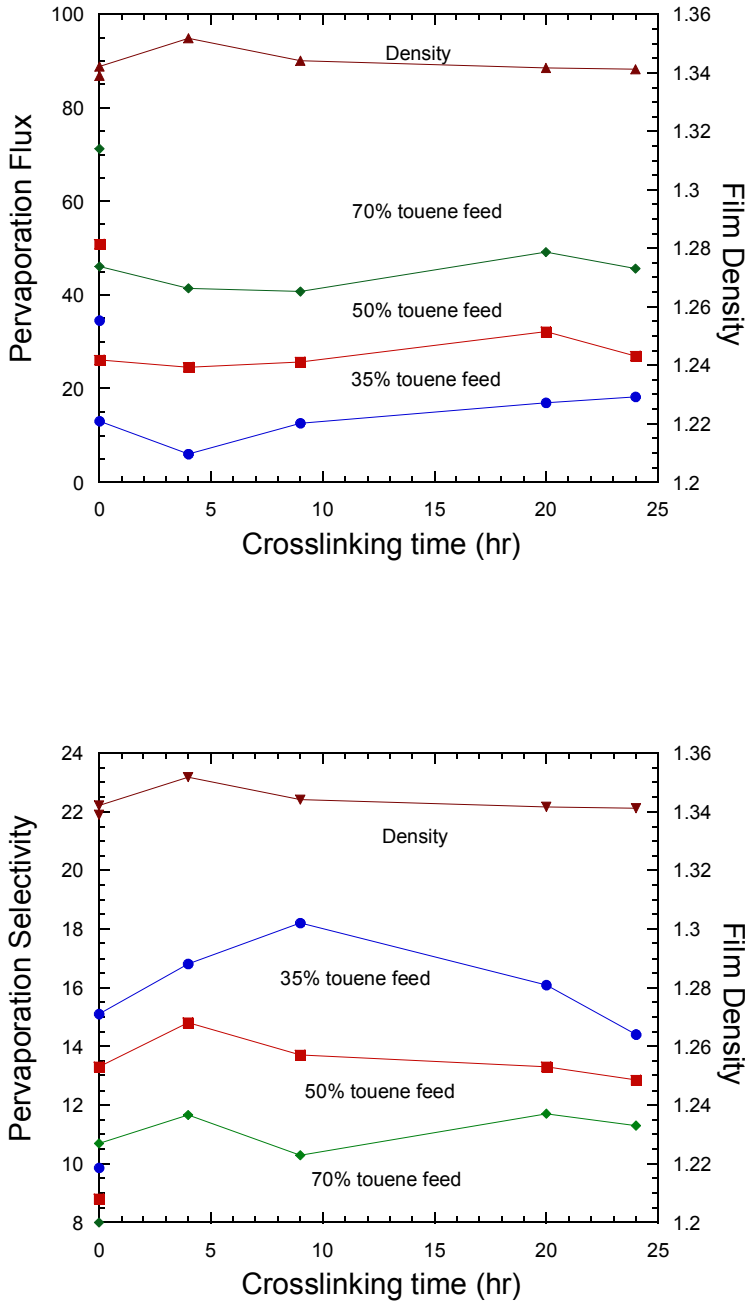


Figure 8.2 Pervaporation performance of thermally imidized 6FDA-DAM/DABA(10%) polyimides crosslinked by ethylene glycol

an electron donor and an electron acceptor. In polyimide membranes, the amide nitrogen atom has higher electron density and is a donor; the carbonyl group has lower electron density and is an acceptor. Charge transfer complex occurs not only between adjacent units in a polymer chain, but also between chains. Polyimide chains may become packed tightly by charge transfer complex interactions as suggested in Figure 8.3.

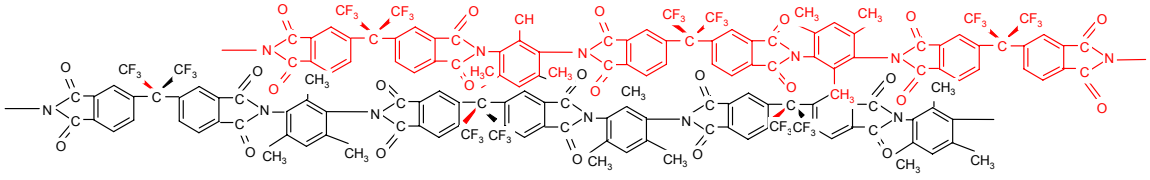


Figure 8.3 Charge transfer complex in polyimide membranes

The annealing effect and charge transfer complex interaction facilitated by high temperature treatment will change chain packing and mass transfer, consequently. To decouple the crosslinking and the thermal treatment, 6FDA-DAM/DABA(10%) membranes were heated at 220°C for 4 hours, 9 hours and 20 hours, respectively. The pervaporation performance is shown in Figure 8.4.

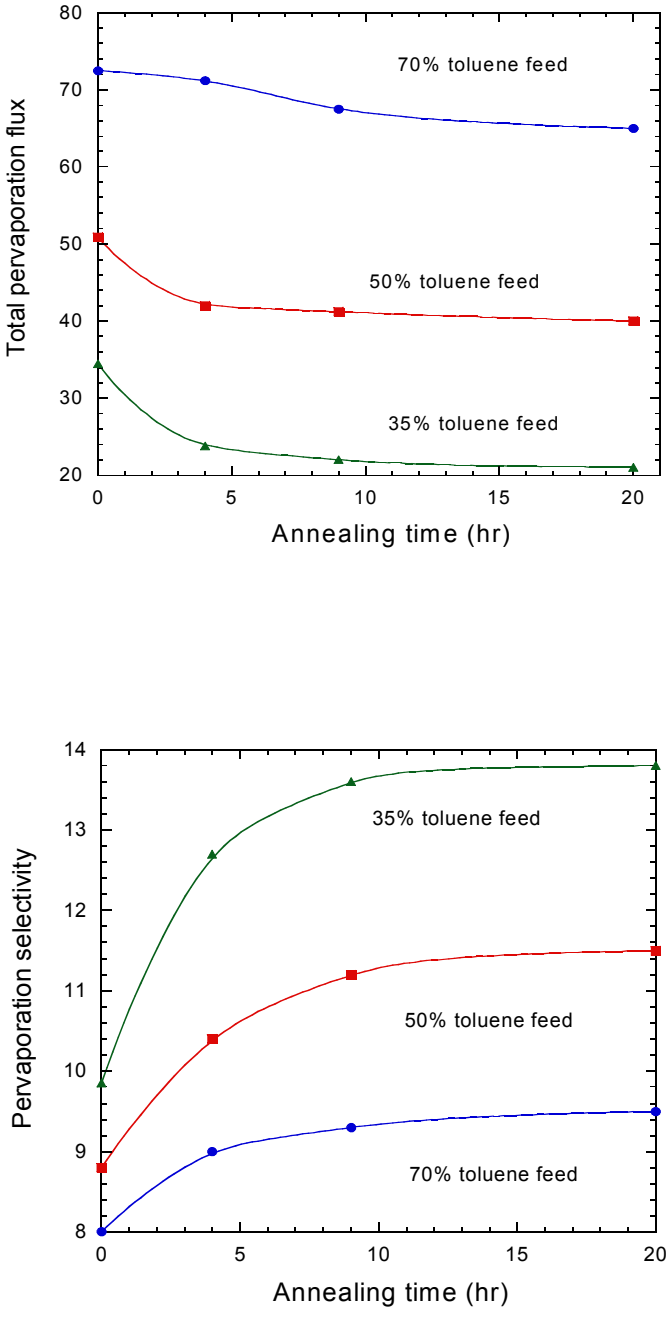
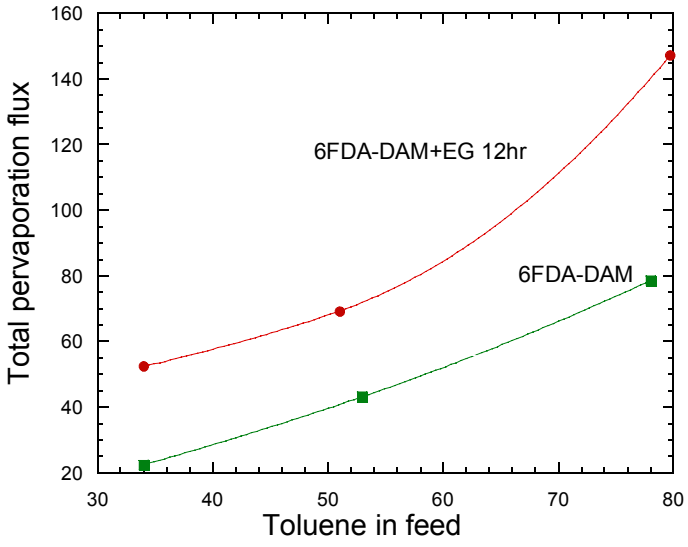


Figure 8.4 Pervaporation performance of 6FDA-DAM/DABA(10%) membranes annealed at 100°C

Thermal treatment of 6FDA-DAM/DABA(10%) increases pervaporation selectivity and decreases pervaporation flux as we expected. The annealing effect is significant when the heating time is under 9 hours. As heating time increases beyond 9 hours, the pervaporation selectivity and flux do not change significantly. Comparing the crosslinking effect in Figure 8.2 and the thermal effect in Figure 8.4, crosslinking has a more significant impact on membrane pervaporation performance than the thermal treatment.

The crosslinking mechanism in scheme 8.1 indicates that ethylene glycol reacts with the carboxylic acid in DABA groups. However, ethylene glycol may involve reactions with other groups, such as non-imidized amic acid, active end group (anhydride). To clarify the side effect of the crosslinking reaction, the 6FDA-DAM polyimide material was treated by the mono-esterification process described in Chapter 3. The treated 6FDA-DAM was cast into film and heated at 220°C for 12 hours. The pervaporation performance is shown in Figure 8.5. After the ethylene glycol treatment, the pervaporation flux increases and the selectivity decreases. The results show that ethylene glycol treatment has an opposite impact on the polyimide materials without the DABA group.

Ethylene glycol treatment of 6FDA-DAM/DABA polyimides has three separate impacts on the polyimide membranes: crosslinking of DABA group in the polyimides, annealing, and side reaction with polyimide chains. Both crosslinking and annealing increase



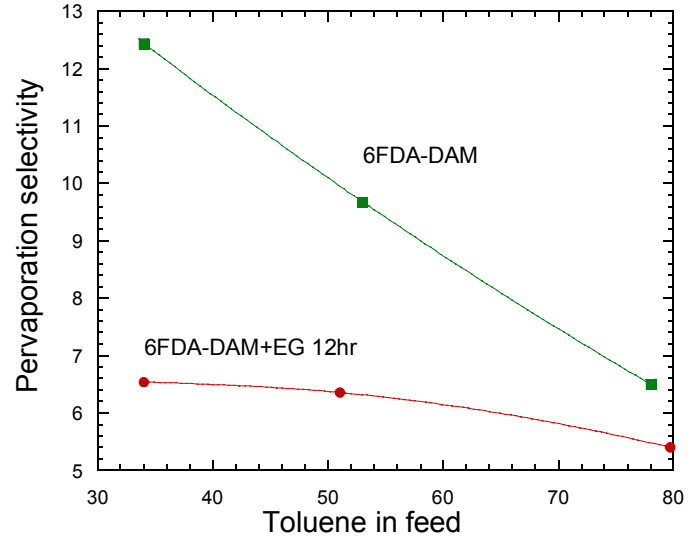


Figure 8.5 Pervaporation performance of ethylene glycol treated 6FDA-DAM membrane

8.5 Sorption of ethylene glycol crosslinked 6FDA/DAM/DABA(10%) membrane

pervaporation selectivity and decrease pervaporation flux; side reactions decrease pervpaoration selectivity and increase pervaporation flux. The pervaporation performance of the ethylene glycol crosslinked 6FDA-DAM/DABA(10%) shown in Figure 8.2 is the output combining the three impacts from the ethylene glycol crosslinking process.

The swelling of ethylene glycol crosslinked 6FDA-DAM/DABA(10%) membrane in toluene at 100°C is shown in Figure 8.6. After the mono-esterification process, the membrane swelling is significantly reduced. The membrane crosslinked for 4 hours has the lowest toluene swelling. However, the toluene swelling of membranes with various crosslinking times does not change significantly. The swelling results agree with the pervaporation performance shown in Figure 8.2.

The sorption of the ethylene glycol crosslinked 6FDA-DAM/DABA(10%) membranes was conducted in 50/50% toluene/iso-octane mixtures at 100°C, and was measured by head-space GC. The solubility selectivity and diffusivity selectivity are shown in Figure 8.7. The significant improvement in the pervaporation selectivity of the 6FDA-DAM/DABA(10%) mono-ester membrane is mainly from the solubility selectivity increase. The membrane crosslinked for 4 hours has the highest pervaporation selectivity, however, with a combination of the lowest solubility selectivity and the highest diffusivity selectivity. As the crosslinking time increases, the pervaporation selectivity starts to decrease slightly with a steady increase in solubility selectivity and a steady decrease in diffusivity selectivity. The results in Figure 8.2 and Figure 8.7 indicate that

from the original 6FDA-DAM/DABA(10%) membrane to the mono-ester membrane, from the mono-ester membrane to the membrane crosslinked for 4 hours, the polymer structures have significant changes, which results in significant changes in the solubility/diffusivity selectivity.

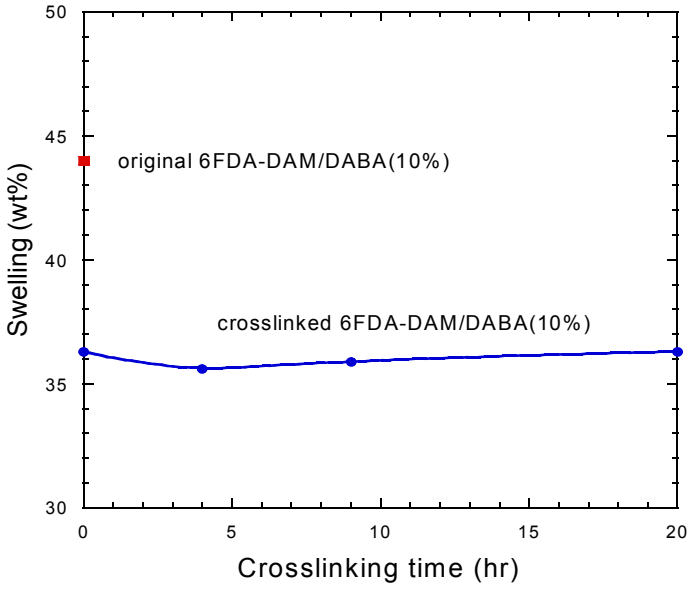


Figure 8.6 Swelling of ethylene glycol crosslinked 6FDA-DAM/DABA(10%) membranes in toluene at 100°C

8.6 Properties of the crosslinked 6FDA-DAM/DABA(10%) polyimides

To further explain the transport properties, the material properties of the 6FDA-DAM/DABA(10%) were measured. The molecular weight of the original and mono-ester 6FDA-DAM/DABA(10%) were measured by GPC with conventional polystyrene

calibration. The results in Table 8.1 show that for successful crosslinking, the molecular weight of the polyimides does not decrease significantly during the mono-esterification. Brittle membranes after the crosslinking are due to the severe molecular degradation in the crosslinking process. The possible reason for the molecular degradation is that the unimidized amic acid is attacked by ethylene glycol or by the catalyst in the high temperature mon-esterification process. As discussed in Chapter 7, the 6FDA-DAM/DABA(10%) polyimides do not have amic acid peaks detected within the NMR sensitivity, while 6FDA-DAM/DABA(33%) polyimides have at least 4% amic acid remaining in the polyimides. This may explain the severe molecular degradation for the 6FDA-DAM/DABA(33%) polyimide after the mono-esterification.

When 6FDA-DAM polyimide was treated with ethylene glycol in the same mono-esterification process described in Chapter 4 as a control, the pervaporation selectivity decreases and flux increases surprisingly as shown in Figure 8.5. The molecular weight of 6FDA-DAM only decreases about 6% after the treatment. However, the polydispersity increases 17%. The ethylene glycol treatment does lead to slight degradation for 6FDA-DAM(without crosslinking site DABA), and the change in the pervaporation performance is due to this degradation.

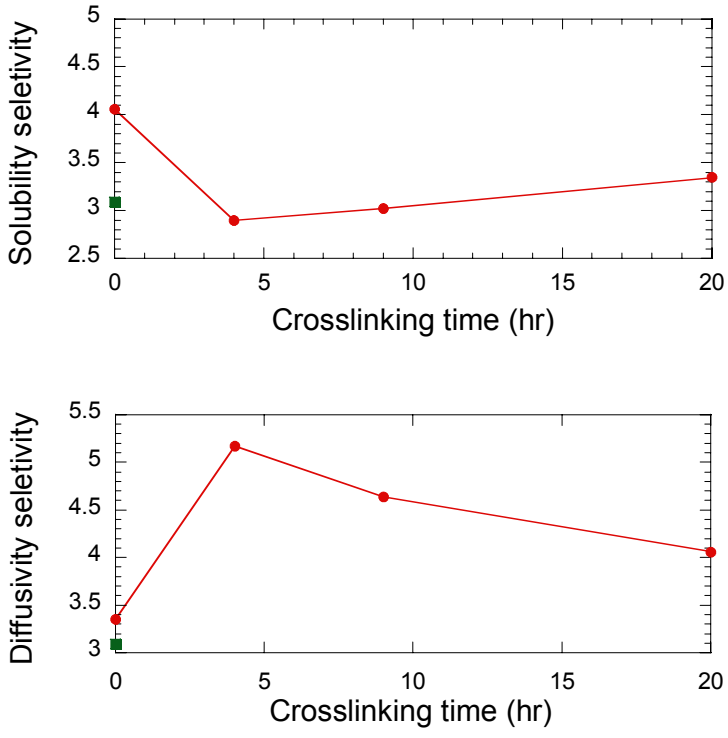


Figure 8.7 Solubility selectivity and diffusivity selectivity of crosslinked 6FDA-DAM/DABA(10%) membrane in 50/50wt% toluene/iso-octane mixtures at 100°C

Table 8.1 Molecular weight of 6FDA-DAM/DABA series polyimides and mono-esters

10%DABA (flexible monoester film)				10%DABA (brittle mono-ester film)				33% DABA (brittle mono-ester film)			
original		mono-ester		original		mono-ester		original		mono-ester	
Mn	Pd	Mn	Pd	Mn	Pd	Mn	Pd	Mn	Pd	Mn	Pd
26520	1.9	22070	1.6	15500	2.8	6900	3.0	26800	2.2	9170	2.8

Table 8.1 Molecular weight of 6FDA-DAM/DABA series polyimides and mono-esters, continued

0% DABA			
original		Mono-ester treatment	
Mn	Pd	Mn	Pd
16690	2.76	15670	3.25

To investigate the structure of the ethylene glycol crosslinked 6FDA-DAM/DABA(10%) polyimides, WAXD was conducted and the spectra are shown in Figure 8.8. The original membrane doesn't have any obvious peaks. The mono-ester membrane has a very large and broad peak. The peak of the membrane crosslinked for 4-hour decreases significantly, and as crosslinking time increases to 9 hours and 20 hours, the peaks start to grow continuously. The dramatic peak changes from the original membrane to the mono-ester membrane to the membrane crosslinked for 4 hours indicate the significant change of chain packing, possibly structure change essentially. These changes agree with the trends in membrane solubility/diffusivity selectivity shown in Figure 8.7. From the mono-ester membrane to the 20-hour membrane, their peaks continue to shift slightly to larger angles, which means smaller d-space and tighter chain packing. However, the membrane density results in Figure 8.2 do not show the same trend since the membrane density decreases slightly when crosslinking time increases.

The glass transition temperature of the ethylene glycol crosslinking 6FDA-DAM/DABA(10%) materials is shown in Table 8.2. The mono-ester and the crosslinked membranes have very similar glass transition temperature. However, all of the three values are lower than that of the original material.

Table 8.2 Glass transition temperature of crosslinking 6FDA-DAM/DABA(10%)

original	372°C
Mono-ester	360°C
4hr crosslinking	358°C
9hr crosslinking	354°C
20hr crosslinking	356°C

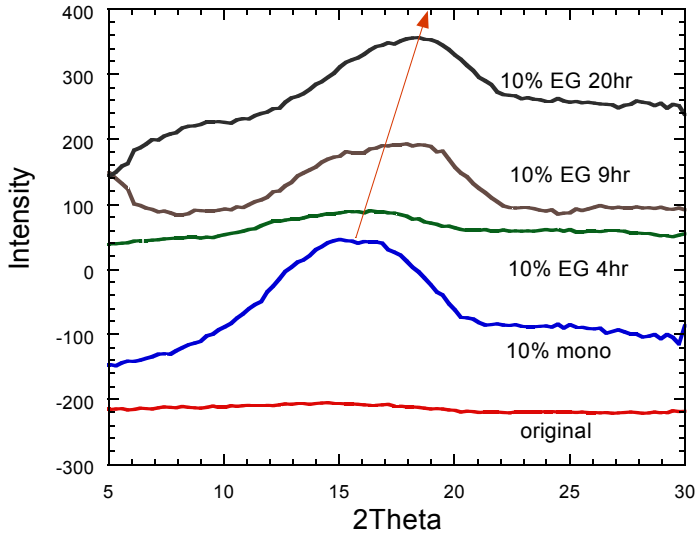
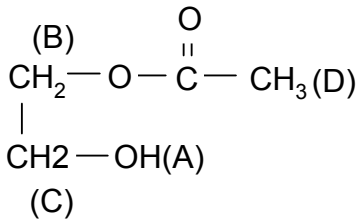


Figure 8.8 WAXD spectra of ethylene glycol crosslinked 6FDA-DAM/DABA(10%) membranes

8.7 NMR spectra of 6FDA-DAM/DABA(10%) ethylene glycol mono-esters

To verify the mono-esterification process, the 6FDA-DAM/DABA(10%) mono-ester solution in d-chloroform was prepared and tested by ^{1}HNMR. The spectrum is compared with those of the original polyimide (Figure 7.5(b)) and 2-hydroxyethyl acetate (Table 8.3) [1]. Figure 8.9 is part of the mono-ester spectrum and peak assignment. However, the characteristic peak 1 and peak 2 are too small to quantify the mono-esterification efficiency.

Table 8.3 [1]HNMR peak assignment of 2-hydroxyethyl acetate (in d-chloroform)



Peak	Shift (ppm)
A	4.30 (small, broad)
B	4.180
C	3.798
D	2.102

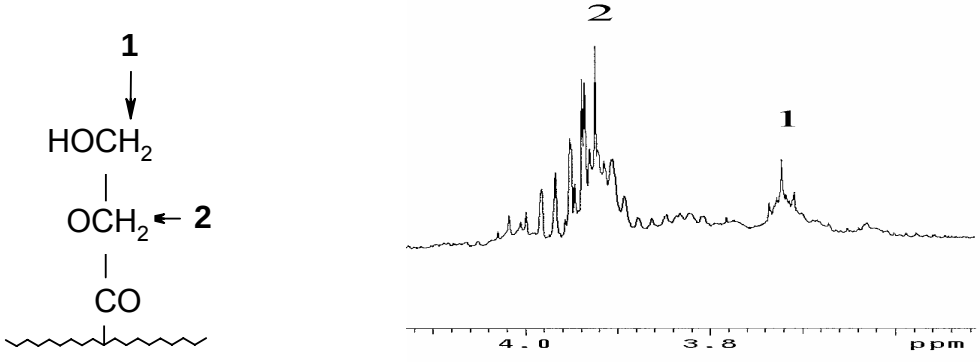


Figure 8.9 The mono-ester peaks of 6FDA-DAM/DABA(10%) ethylene glycol mono-ester

References

1. Spectral databases for organic compounds SDBS

http://www.aist.go.jp/RIODB/SDBS/cgi-bin/direct_frame_top.cgi?lang=eng

Chapter 9 Structure-properties relations of 6FDA-6FpDA/DABA polyimides

Gas permeation studies have shown that membranes made from the 6FDA-6FpDA/DABA series of polyimides display lower CO_2 permeability and higher CO_2/CH_4 selectivity compared to the 6FDA-DAM/DABA series [1, 2]. However, Table 9.1 shows that 6FDA-6FpDA/DABA membranes have a lower solubility parameter and higher fraction free volume than the 6FDA-DAM/DABA series do. This doesn't agree with the general structure-transport relations for gas permeation: lower solubility parameter or higher fraction free volume implies higher gas permeability and lower selectivity.

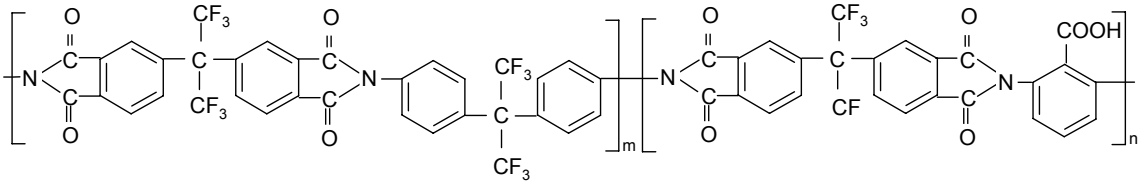


Figure 9.1 Chemical structure of 6FDA-6FpDA/DABA polyimides

Table 9.1 Gas permeation and physical properties of polyimide membranes

Polyimide	Solubility parameter $(J/cm^3)^{1/2}$	Tg(ºC)	Density (g/cm^3)	Free Volume	P_{CO2} (Barrer)	α CO_2/CH_4
6FDA-DAM[3]	26.4	377	1.352	0.182	431	17
6FDA-6FpDA[2]	24.1	320	1.466	0.190	63.9	39.9

To explore the structure-transport relations of the 6FDA-6FpDA/DABA membranes, pervaporation and sorption tests of the 6FDA-6FpDA/DABA membranes were conducted and compared to those of the 6FDA-DAM/DABA membranes. 6FDA-6FpDA was purchased from Celanese, 6FDA-DAM, 6FDA-DAM/DABA(33%) and 6FDA-6FpDA/DABA(33%) were synthesized in this lab by the chemical imidization method described in Chapter 3. Figure 9.2 and Figure 9.3 suggest that similar to the gas permeation scenario, the 6FDA-6FpDA/DABA series membranes show significantly higher pervaporation selectivity, lower flux and lower swelling than their 6FDA-DAM/DABA counterparts. The sorption results in Table 9.2 show that both solubility selectivity and diffusivity selectivity of 6FDA-6FpDA/DABA series membranes are higher than those of 6FDA-DAM/DABA membranes. The fractional free volume data in Table 9.3 clearly show that the fractional free volume of 6FDA-6FpDA/DABA membranes is higher than that of 6FDA-DAM/DABA membranes.

To understand the unique mass transport properties of 6FDA-6FpDA/DABA membranes, the structure of 6FDA-DAM/DABA and 6FDA-6FpDA/DABA membranes were studied. The WAXD spectra of 6FDA-DAM and 6FDA-6FpDA in Figure 9.4 show that 6FDA-DAM membranes have only one peak with a d-spacing of 5.6 Å, while 6FDA-6FpDA membranes have two peaks with d-spacings of 5.7 Å and 3.5 Å, respectively. The 6FDA-DAM has a simple chain packing, while 6FDA-6FpDA has a complicated chain packing. Though 6FDA-6FpDA has a higher fractional free volume than 6FDA-DAM, the mass

transport properties in gas permeation and pervaporation, to some degree, reflect the distribution of free volume.

Free volume is a widely used concept to correlate structure-transport relations. In most cases, the average free volume calculated by the measurement of film density, can be used to explain most trends. However, for some polymers like 6FDA-6FpDA, the free volume distribution in addition to the absolute free volume affects their transport properties. Free volume distribution can be measured by Positron Annihilation Lifetime Spectroscopy (PALS). For some polymeric and composite membranes, PALS results explain their structure-transport relations very well [6].

Free volume distribution can also be calculated by computer simulation techniques. Figure 9.5 is a preliminary simulation of 6FDA-6FpDA chain packing [7]. It clearly shows two types of regional packing: region A and region B. This may explain the WAXD spectra in Figure 9.3. In recent years free volume distribution of some glassy polymers, including polyimides, which are widely used in gas permeation research, has been calculated by computer simulation. The simulated cavity size distribution of 6FDA-6FpDA is a broad, continuous peak with an average cavity size of 6.76 Å [8].

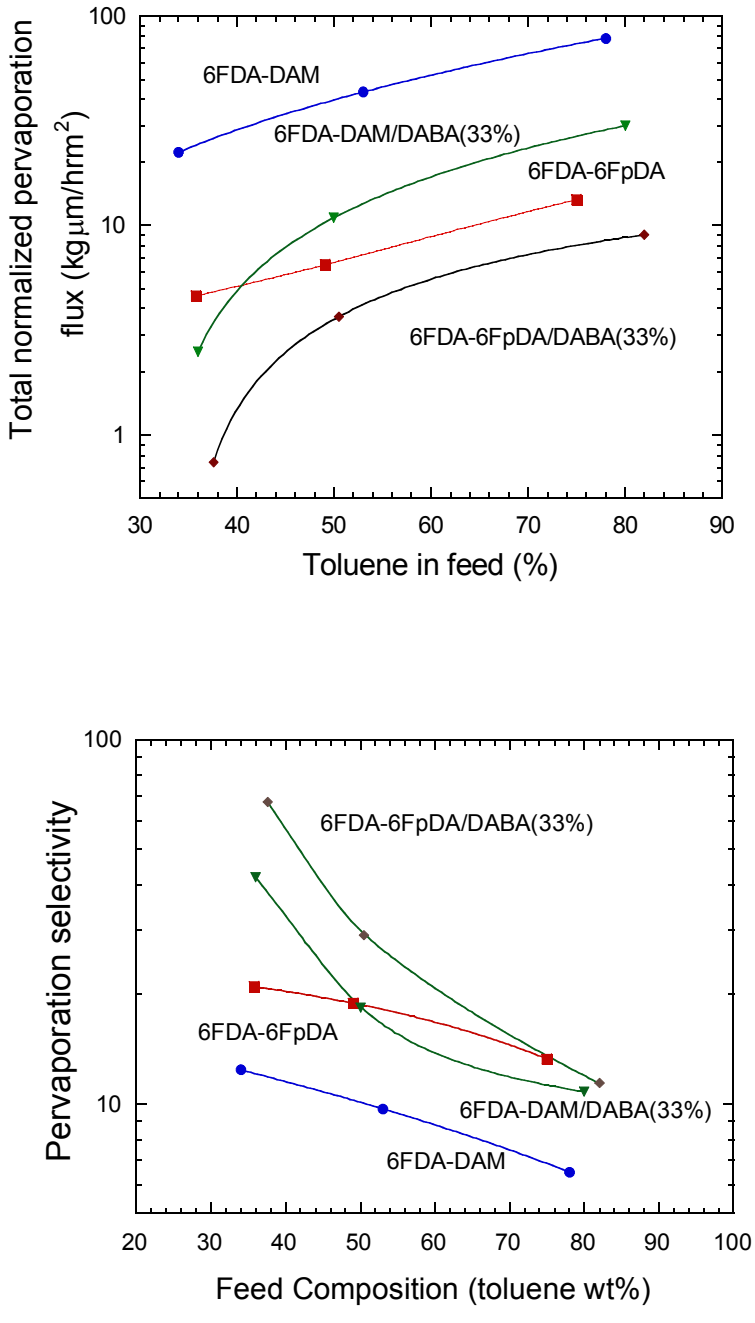


Figure 9.2 Pervaporation of 6FDA-DAM/DABA and 6FDA-6FpDA/DABA series membranes in toluene/iso-octane mixtures at 100°C

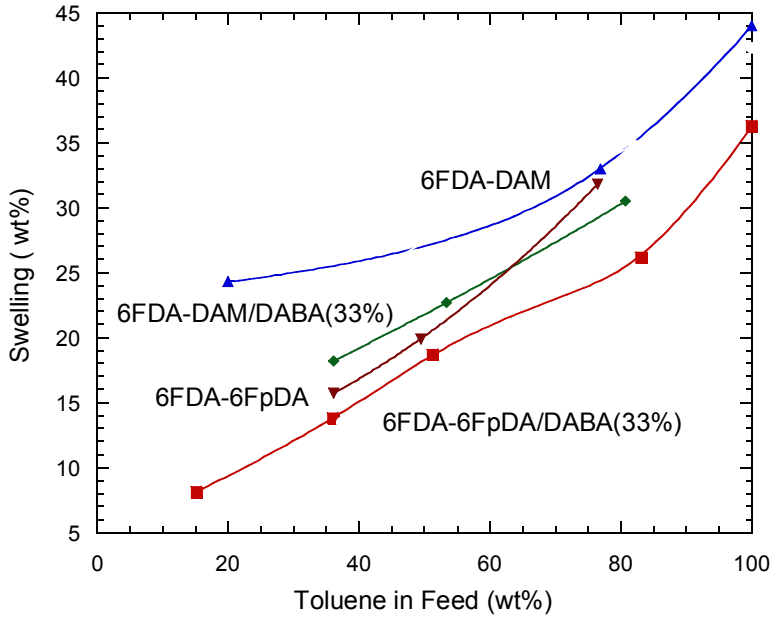


Figure 9.3 Swelling of 6FDA-DAM/DABA and 6FDA-6FpDA/DABA membranes in toluene/iso-octane mixtures at 100°C

The structure-transport relationships for the 6FDA-6FpDA/DABA series membranes are a very interesting topic for future research. Such research could combine membrane permeation experiments for small gases, such as H_2, O_2, large gases like CO_2, and organic liquid, polymer characterizations, such as PALS, and computer simulation. The research may lead to more comprehensive conclusions about membrane transport, such as the free volume distribution-transport relation, free volume distribution characterization, and important guidelines for future membrane research.

Table 9.2 Solubility/diffusion selectivity in toluene/iso-octane (50/50) at 100°C

Polyimides	Solubility Selectivity	Diffusivity Selectivity
6FDA-DAM	3.2	3.0
6FDA-6FpDA	3.6	5.3
6FDA-DAM/DABA (33%)	4.5	4.7
6FDA-6FpDA/DABA (33%)	5.0	5.8

Table 9-3 Membrane film density and fraction free volume

Polyimides	Film Density (g/cm^3)	Fraction free volume
6FDA-DAM	1.338	0.190
6FDA-6FpDA	1.455	0.196
6FDA-DAM/DABA (33%)	1.380	0.184
6FDA-6FpDA/DABA (33%)	1.448	0.196

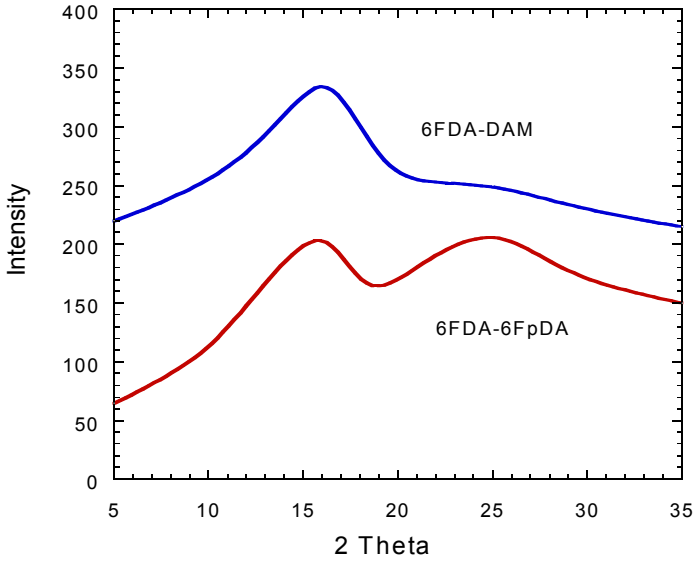


Figure 9.4 WAXD spectra of 6FDA-DAM and 6FDA-6FpDA membranes

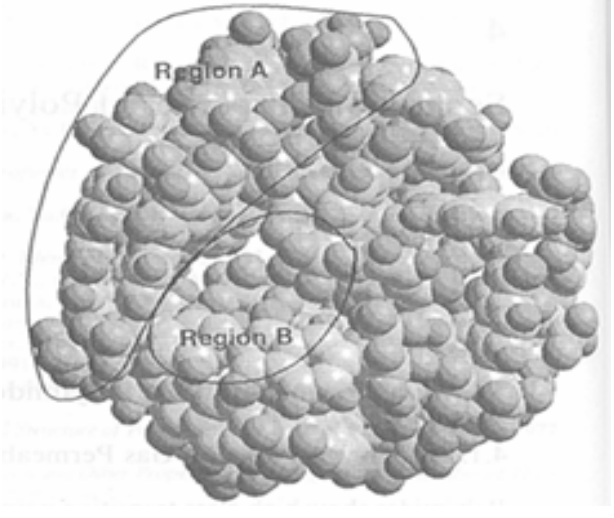


Figure 9.5 Simulated 6FDA-6FpDA chain packing
Source: Polyimide Membrane Application, Fabrication and Properties, H.Ohya et al., Gorgon and Breath, 1996, p111

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Chapter 10 Ionic crosslinking of DABA containing polyimides

10.1 Background

Crosslinking is a common method to modify the chemical and physical structure of membranes in order to improve thermal, mechanical and transport properties. In Chapter 8 the carboxylic acid groups in the DABA units in the polyimides were crosslinked by ethylene glycol with covalent bonds. The carboxylic acid can also be crosslinked by ionic bonds. Polyacrylic acid (PAA) is a common polymer for pervaporation separation of water-ethanol mixtures. PAA has a high charge density based on the carboxyl groups, which are available for crosslinking and salt-formation with alkaline metals. Zhao and Huang investigated PAA-nylon 66 blend membranes [1]. A multivalent cation Al^{3+} was used to induce ionic crosslinking to improve PAA resistance to aqueous solutions. Figure 10.1 shows the nature of the crosslinking. PV results indicated that both PAA content in the blend and crosslinking degree (varied by controlling crosslinking time) have optimum level. The PV performance was determined not only by hydrophobicity/hydrophilicity of the membranes, but also by the membrane density and morphology.

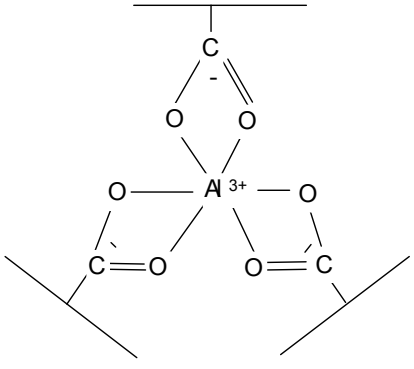


Figure 10.1 Nature of ionic crosslinking

Inui etc. crosslinked poly(methacrylate-methacrylic acid)(MMA-MAA) with Fe^{3+} and Co^{2+} for pervaporation separation of benzene/cyclohexane mixtures [2]. It was found that the permeability of PMMA-PMAA increased with the increasing amounts of metal ion in the membrane. However, for selectivity, the metal concentration in the membrane had an optimum. Addition of ions made the membrane less hydrophobic. Consequently the benzene permeability increased as well as the selectivity because benzene is less hydrophobic compared to cyclohexane. When the metal concentration in the membrane was high, the metal ions were proposed to act as an apparent 'plasticizer' as well as a crosslinking regent. Both benzene and cyclohexane permeability increased, but the selectivity decreased. The hypothetical structure of such crosslinked membranes is shown in Figure.10.2. This explanation was supported by contact angle data and measurement of the glass transition temperature.

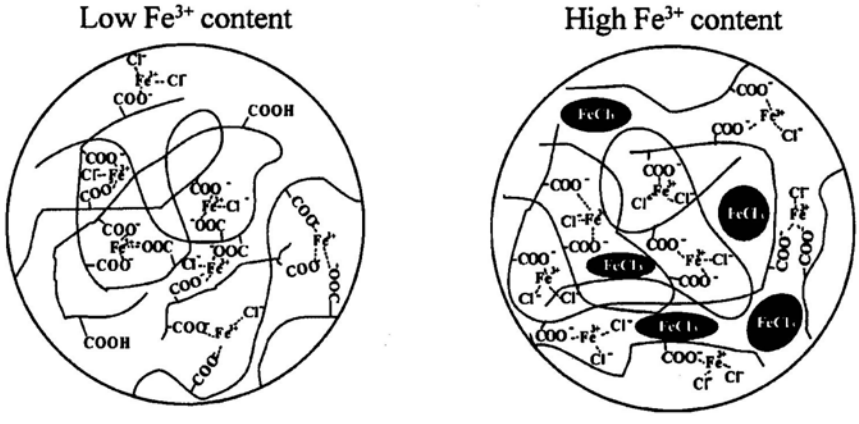


Figure 10.2 Structure of MMA-MAA membranes with high and low metal ion contents

Source: K. Inui, etc, J.Appl.Polymer Sci., 71(1999), 233-241

Ho etc. crosslinked polycarbonate membranes made from bisphenol A with copper acetylacetonate and improved the pervaporation selectivity of toluene/iso-octane significantly [3]. Matsui etc. crosslinked poly(n-alkyl acrylate-acrylic acid) with aluminum acetylacetonate (AlAcAc) for pervaporation separation of toluene/iso-octane mixtures. Before the crosslinking, the membranes are over-swelled in toluene/iso-octane mixtures and cannot endure the pervaporation test. The crosslinking reduced the swelling, improved the mechanical properties of the membranes and duration of use in the toluene/iso-octane mixtures, and gave acceptable pervaporation performance [4, 5].

Compared to the two-step high temperature ethylene glycol crosslinking discussed in Chapter 8, ionic crosslinking process is simple, quick and at possible mild temperatures. In this Chapter, 6FDA-DAM/DABA and 6FDA-6FpDA/DABA membranes were crosslinked by aluminum acetylacetonate, and their material properties, pervaporation and sorption performance were discussed.

The AlAcAc crosslinking was made by dissolving calculated amounts of polyimide and AlAcAc in THF, and casting the solution on a Teflon plate. The cast membrane was dried in vacuum at 60°C for 12 hours, then further dried at 120°C for another 12 hours to finish the crosslinking.

10.2 Pervaporation and sorption of AlAcAc crosslinked 6FDA-DAM/DABA

According to the idealized crosslinking mechanism in Figure 10.1, one aluminum cation attracts three carboxylic acid anions. The stoichiometric AlAcAc versus DABA ratio is 1:3 (mole/mole). Two different AlAcAc/DABA ratios were used in the crosslinking. As the AlAcAc/DABA ratio is 1, the amount of AlAcAc in the membrane is in significant excess. The excess amount of AlAcAc may act as a plasticizer as well as a crosslinker as shown in Figure 10.2. As the Al/DABA ratio is 0.22, some of the DABA groups in the membrane may be not crosslinked. The pervaporation performance of ionic crosslinked 6FDA-DAM/DABA(33%) is shown in Figure 10.3. The ionic crosslinked 6FDA-DAM/DABA(33%) membranes have higher flux and lower selectivity than the original 6FDA/DABA(33%) membrane. AlAcAc acts as a plasticizer no matter what the AlAcAc content in the membrane, below or above the stoichiometric ratio.

Since AlAcAc acts as a plasticizer in the 6FDA-DAM/DABA membranes, the plasticization could be used in some highly selective membranes, such as 6FDA-DAM/DABA(60%), to increase flux significantly with some sacrifice of selectivity to improve the performance. Figure 10.4 is the pervaporation performance of 6FDA-DAM/DABA(60%) crosslinked by AlAcAc with AlAcAc/DABA ratio of 1.0. The performance comparison of the AlAcAc crosslinked 6FDA-DAM/DABA membranes is plotted in Figure 10.5. All the data in the figure were taken at 100°C in 50/50 wt% toluene/iso-octane mixtures. The round dots are literature data. A trade-off line is drawn.

The 6FDA-DAM/DABA and the AlAcAc crosslinked membranes are all slightly below the trade-off.

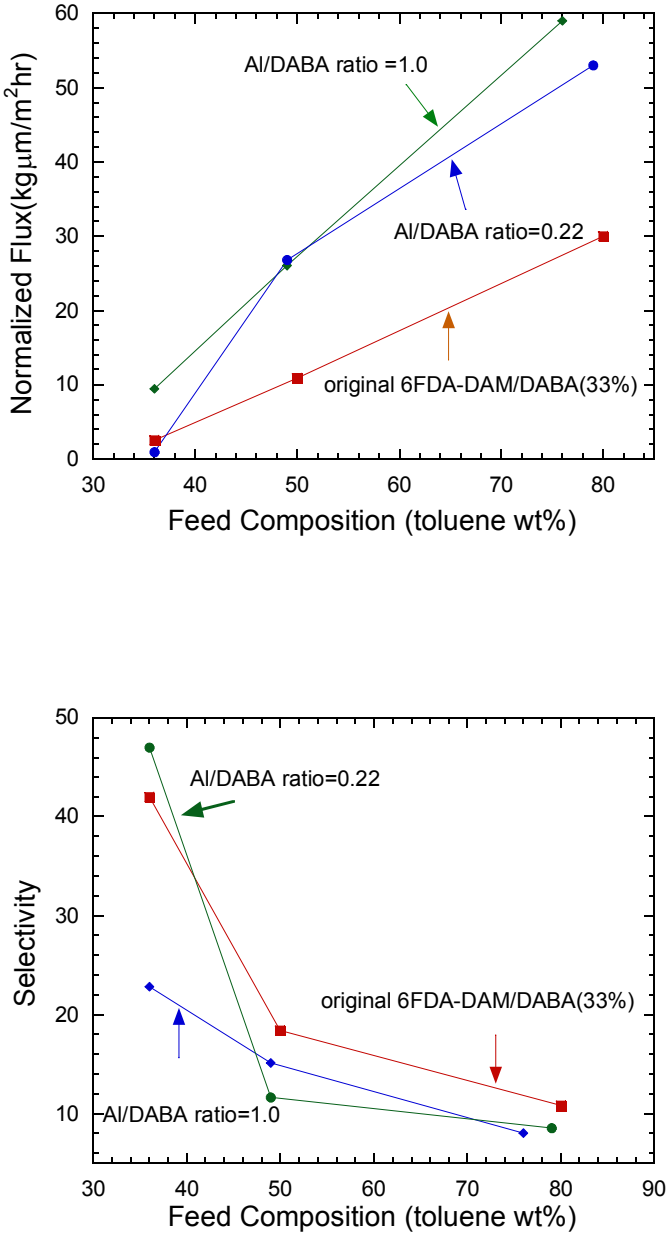
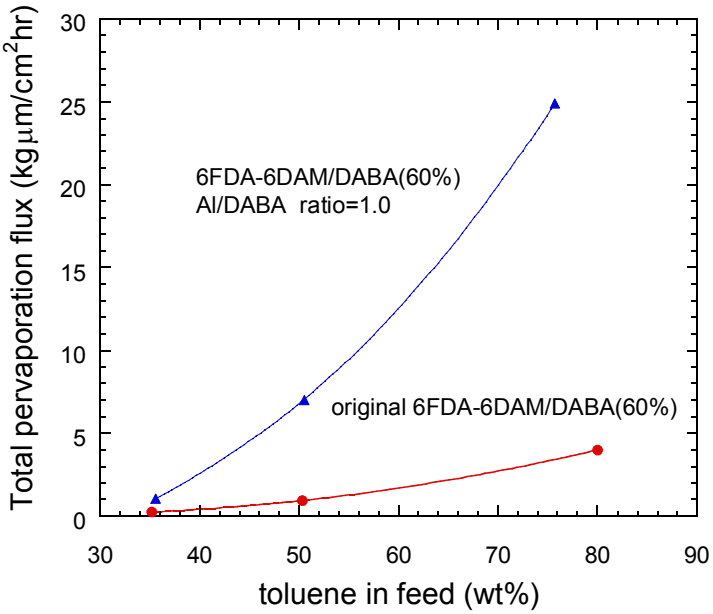


Figure 10.3 Pervaporation of 6FDA-DAM/DABA(33%) crosslinked by AlAcAc



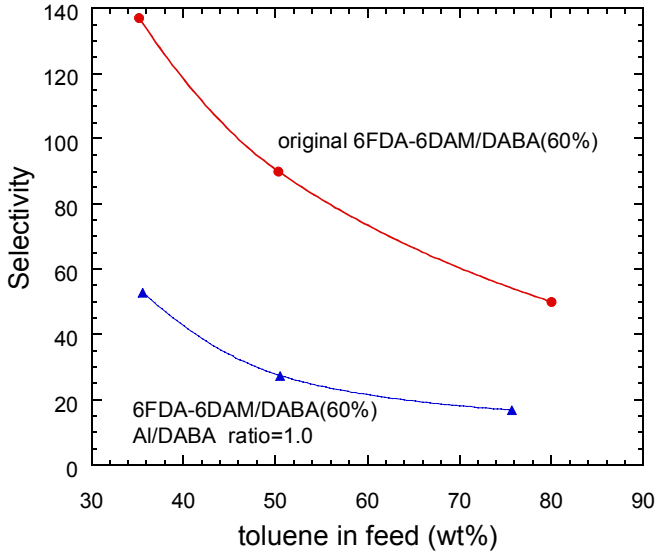


Figure 10.4 Pervaporation of 6FDA-DAM/DABA(60%) crosslinked by AlAcAc with AlAcAc/DABA ratio 1.0(mole/mole)

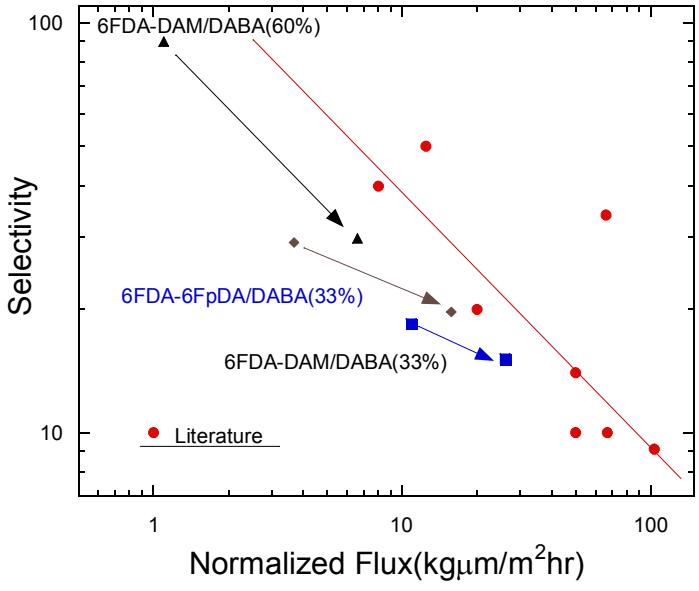


Figure 10.5 Performance comparison of AlAcAc crosslinked 6FDA-DAM/DABA membranes

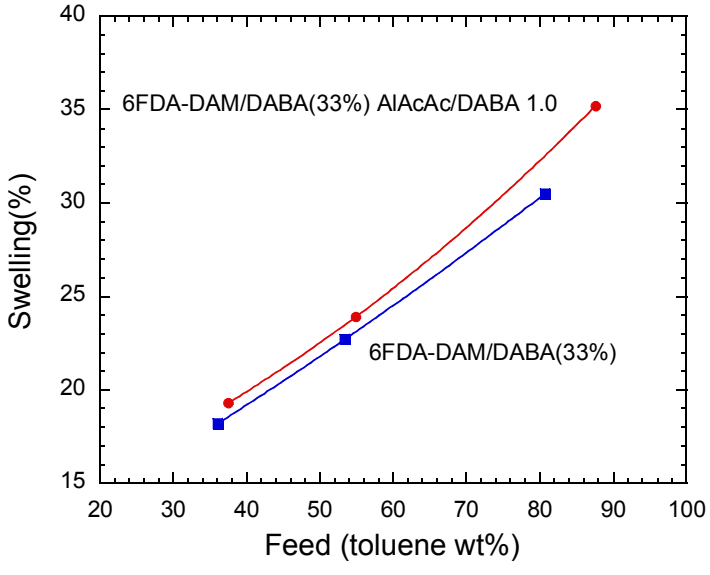


Figure 10.6 Total swelling of AlAcAc crosslinked 6FDA-DAM/DABA(33%) in toluene/iso-ocatne mixtures at 100°C

line. The AlAcAc plasticization pushes the membrane performance slightly closer to the trade-off line.

Table 10.1 Film density and solubility/diffusion selectivity in toluene/iso-octane(50/50) at 100°C

Polyimides	Solubility Selectivity	Diffusivity Selectivity	Film density (g/cm^3)
6FDA-DAM/DABA(33%)	4.5	4.7	1.384
6FDA-DAM/DABA(33%) Al/DABA ratio=1.0	4.6	3.8	1.377
6FDA-DAM/DABA(33%) Al/DABA ratio=0.22	4.5	2.5	1.365

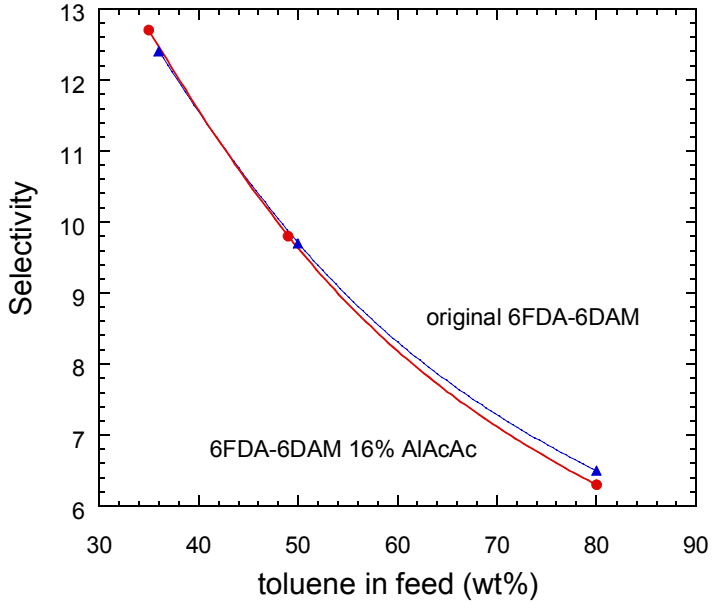
The total swelling of the 6FDA-DAM/DABA(33%) with the AlAcAc/DABA ratio of 1.0 in toluene/iso-octane mixtures at 100°C is slightly higher than the original 6FDA-DAM/DABA(33%) membrane as shown in Figure 10.6. The film density of the AlAcAc treated membranes is lower than that of the original membrane. The sorption tests show that after the AlAcAc treatment, the solubility selectivity of the membranes does not change within the error range, while the diffusivity selectivity decreases significantly. The swelling and film density agree with the pervaporation data. The sorption tests show that the decrease in the pervaporation selectivity is due to the decrease in diffusivity selectivity.

10.3 Reaction mechanism discussion

The 6FDA-DAM is treated with 16 wt% AlAcAc by the process described in 10.1 as a control. The 16 wt% AlAcAc in the membrane is the same amount of AlAcAc for the 6FDA-DAM/DABA(33%) with the AlAcAc/DABA ratio of 1.0. The pervaporation performance of the treated 6FDA-DAM membrane is very similar to the original as shown in Figure 10.7. AlAcAc does not react with the 6FDA-DAM membrane, which does not have any active sites for AlAcAc.

In Reference [3] and Reference [4, 5], CuAcAc and AlAcAc successfully crosslinked polycarbonate and Poly(acrylate-acrylic acid) respectively. However, for the 6FDA-DAM/DABA membranes, AlAcAc acts as a plasticizer, and possible reason is that in the literature, the crosslinking temperature is above the glass transition temperature of the membranes. In our studies, the glass transition temperature of 6FDA-DAM/DABA is too high to be reached in the lab. The crosslinking temperature is set at 120°C, which is the boiling point of the assumed crosslinking side product-acetylactone. A higher temperature crosslinking at 220°C was conducted. The 6FDA-DAM/DABA(33%) membrane was brittle after the treatment. In DSC tests no glass transition temperature is observed for the AlAcAc treated membranes.

For the 6FDA-DAM/DABA membranes any benefits of ionic crosslinking provided by AlAcAc is the offset by the plasticization effect. The interactions involved in these systems are not clear yet, and should be studied more fully.



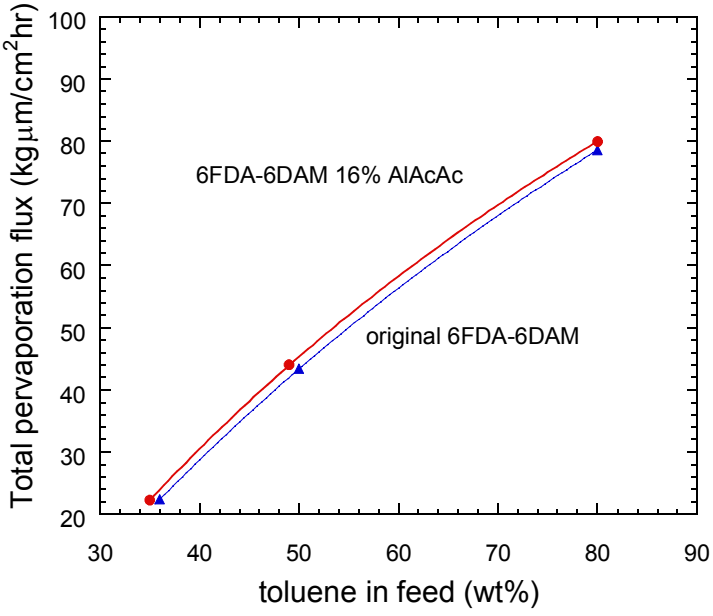


Figure 10.7 Pervaporation performance of AlAcAc treated 6FDA-DAM

10.4 Pervaporation performance comparison

The pervaporation performance of the polyimide membranes discussed in this study is compared with literature data. All the data are taken in 50/50 wt% toluene/iso-octane mixtures at 100°C. As shown in Figure 10.8, among all the membranes involved in this study, three membranes have the best pervaporation performance. They are chemically imidized 6FDA-DAM/DABA(33%) with AlAcAc treatment (AlAcAc/DABA ratio is 1.0), chemically imidized 6FDA-DAM/DABA(10%) with ethylene glycol crosslinking, and thermally imidized 6FDA-DAM/DABA(10%) with ethylene glycol crosslinking, respectively. The AlAcAc acts as a plasticizer for the first membrane. If it is proved that AlAcAc in the membrane is stable in long-term pervaporation tests, it could be used to treat the thermally imidized 6FDA-DAM/DABA(33%) membranes to improve pervaporation performance. For ethylene glycol crosslinking, the crosslinking of 6FDA-DAM/DABA(33%) membrane needs more study. If the flexible membranes could be made after the crosslinking, the membrane performance would have further improvement.

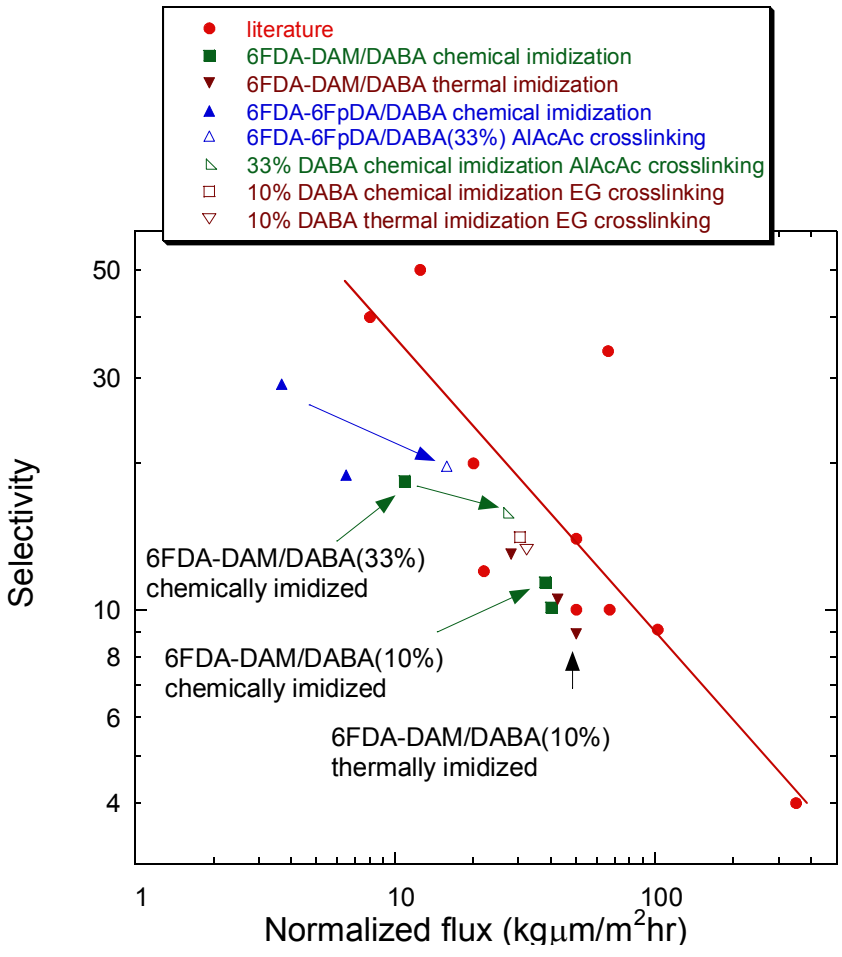


Figure 10.8 Pervaporation performance comparison of polyimide membranes used in this study

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Chapter 11 Conclusions and recommendations

11.1 Conclusions

1. The introduction of DABA groups to the polyimide structure facilitates chain packing, reduces membrane swelling, increases pervaporation selectivity, and decreases pervaporation flux for toluene/iso-octane mixtures.

2. The thermal imidization process produces polyimides with a higher degree of imidization than chemical imidization does. As a result, chemical imidization leads to a higher percentage of carboxylic acid units than thermal imidization does. Chemical imidization leads to membranes with higher film density, higher glass transition temperature and lower pervaporation flux and higher selectivity in toluene/iso-octane mixtures than the thermally imidized membranes because of the higher carboxylic acid concentration.

3. The chemically imidized 6FDA-DAM/DABA(10%) membranes are slightly brittle after ethylene glycol crosslinking. Only the thermal imidization 6FDA-DAM/DABA(10%) membranes have good flexibility. The pervaporation selectivity of these membranes improves significantly after the ethylene glycol crosslinking. The 6FDA-DAM/DABA(33%) membranes after the crosslinking were too brittle to endure pervaporation tests.

4. For the original 6FDA-DAM/DABA polyimides, both membranes from chemical imidization and thermal imidization are good for pervaporation practice. However, for the ethylene glycol crosslinking, only the thermal imidization polyimides form flexible membranes after the crosslinking.

5. Solubility selectivity and diffusivity selectivity of the 6FDA-DAM/DABA membranes have general linear relations with solubility parameters and inverse of fractional free volume, respectively. The structure-mass transport relations show that for the 6FDA-DAM/DABA membranes, both solubility selectivity and diffusivity selectivity contribute to the pervaporation selectivity. For the chemically imidized membranes, an increase in DABA concentration has a positive effect on solubility selectivity and diffusivity selectivity. For the thermal imidization membranes, an increase in DABA concentration has a significant effect on diffusivity selectivity only.

6. The 6FDA-6FpDA/DABA membranes have higher pervaporation selectivity and lower pervaporation flux than the 6FDA-DAM/DABA membranes. However, the 6FDA-6FpDA/DABA membranes have lower solubility parameters and slightly higher fractional free volume than the 6FDA-DAM/DABA membranes. The WAXD spectra and the computer simulated chain packing [1] suggest that in some scenario, the free volume distribution is a better characterization than the average fractional free volume to determine membrane transport properties.

7. The aluminum acetylacetonate(AlAcAc) treatment of 6FDA-DAM/DABA polyimides to give ionic crosslinking seems to lead to increased platicization by toluene [2, 3, 4, 5]. It may be due to the high glass transition temperature and rigidity of the polyimides in this study.

11.2 Recommendations

1. polyimide synthesis

The polyimide synthesis is a complicated process. Some synthesis conditions, such as, imidization method, imidization temperature, imidization time, have significant impact on the degree of imidization, molecular weight, polyimide color and solubility. These physical properties affect membrane transport performance.

In this study, chemical imidization were conducted at 100°C for 1 hour. The 6FDA-DAM/DABA(33%) imidized at these conditions has about 15% amic acid remaining in the polyimide. In future studies, 60-70°C and 3-4 hours are recommended for the imidization process to further the imidization. For the 6FDA-DAM/DABA polyimides, high temperature and long imidization time produce polymers with dark color and lower solubility due to the charge transfer complex and possible hydrogen bonding between carboxylic acid groups. The imidization temperature should always be under 100°C.

2. Imidization process, imidization temperature and molecular weight

Different imidization processes have a significant effect on the structure and properties of the synthesized polyimide. In this study, the impact on the degree of imidization is discussed. Other possible impacts should be studied in the future research.

At the same time, imidization temperature and molecular weight also have important effect in physical properties and transport properties. In chemical imidization, higher temperature results in dark polyimides. The effect of the color in the membrane physical and transport properties could be quantified in future research. The molecular weight effect is mentioned in Chapter 6. A systematic study of the effect of molecular weight on properties, and the possible reason for these effects would also be a topic for future research.

3. Covalent crosslinking

In this study ethylene glycol crosslinking is successful for the 6FDA-DAM/DABA(10%) membranes only. The 6FDA-DAM/DABA(33%) membranes are too brittle for pervaporation tests after the crosslinking. However, previous research shows that 6FDA-DAM/DABA(33%) ethylene glycol crosslinking is successful for gas permeation tests [6]. Though pervaporation tests require membranes with higher flexibility and mechanical strength than gas permeation because of its higher swelling and flux, the degradation of the 6FDA-

DAM/DABA(33%) during the mono-esterification is an issue worth to explore in future research. According to the pervaporation experiments done in this study, the minimum molecular weight required for a flexible 6FDA-DAM/DABA membrane for toluene/iso-octane pervaporation is about 15000(number average molecular weight). The molecular weight of the current 6FDA-DAM/DABA(33%) mono-ester is about 9200. The molecular weight of the mono-esters could improve either by increasing that of the original polyimides or by adjusting the amount of catalyst used in the mono-esterification process.

4. Structure-property relations

In this study the solubility selectivity-solubility parameter and diffusivity selectivity-inverse fractional free volume are correlated for the 6FDA-DAM/DABA membranes. When the 6FDA-6FpDA/DABA membranes are included to expand the correlations, discrepancies are observed. Characteristic parameters other than solubility parameter and fractional free volume are needed to establish extensive correlations between the material structure and transport properties.

References

1. Polyimide Membrane Application, Fabrication and Properties, H.Ohya et al., Gorgon and Breath, 1996, p111
2. K. Inui, T. Noguchi, T. Miyata, T. Uragami, Pervaporation characteristics of methyl methacrylate-methacrylic acid copolymer membranes ionically crosslinked with metal ions for a benzene/cyclohexane mixture, J. Appl. Polymer Sci., 71(1999), 233-241
3. G. Sartori, W.S. Ho, D.W. Savage, R.E. Noone, R.P. Mastondrea, Non-poros polycarbonate membranes for separation of aromatics from saturates, US Patent 5,019,666 (1991)
4. S. Matsui, and D.R. Paul, Pervaporation of aromatic/aliphatic hydrocarbons by crosslinked poly(methyl acrylate-acrylic acid) membranes, J. Membrane Sci., 195(2002), 229-245
5. S. Matsui, D.R. Paul, Pervaporation separation of aromatic/aliphatic hydrocarbons by a series of ionically crosslinked poly(n-alkyl acrylate) membranes, J. Membrane Sci., 213 (2003), 67-83
6. J.D. Wind, Improving Polyimide Membrane Resistance to CO2 Plasticization in Natural Gas Separations. PhD Dissertation, The University of Texas at Austin, 2002

Appendix 1 Definition of selectivity in pervaporation

Because of the phase change that occurs during pervaporation, α_{perv} as defined in the text is not solely an intrinsic property of the membrane material, but also includes the vapor-liquid equilibrium characteristics of the feed mixture. Thus, the membrane selectivity might be defined in a way to exclude the latter effect and to be consistent with the selectivity defined in gas permeation [1], i.e.

$$\alpha_{mem} = \frac{P_i}{P_j} \tag{1}$$

$$P_i = \frac{l \cdot flux_i}{\Delta p_i} \tag{2}$$

where P_i is permeability of component i which is normalizied by the partial pressure (or fugacity) difference between the upstream and downstream for component i, Δp_i. This partial pressure difference provides the driving force for permeation, and in pervaporation, the downstream partial pressure is typically negligible due to the vacuum condition maintained there for most experimental situations. The upstream partial pressure p_i is given by

$$p_i = p_i^{sat} x_i \gamma_i \tag{3}$$

where p_i^{sat} is the saturated vapor pressure of component i at the operation temperature, x_i is the mole fraction of component i in the feed, and γ_i is the activity coefficient. In this work, activity coefficients were calculated from the NRTL equation [2] using parameters

from the compilation of Gmehling et al [3]. In this scheme, the membrane solubility selectivity and diffusivity selectivity are defined as

$$\alpha'_S = \frac{S_i}{S_j} \tag{4}$$

where $$S_i = \frac{\textit{amount of sorption } i}{\textit{dry film mass} \cdot p_i} \tag{5}$$

in which p_i corresponds to the partial pressure that would be in equilibrium with the liquid phase in contact with the membrane surface. In analogy with equation (5), we have

$$\alpha'_D = \alpha_{mem} / \alpha'_S \tag{6}$$

The various selectivities are interrelated by

$$\alpha_{mem} = \alpha_{perv} / \alpha_{evap} \tag{7}$$

$$\alpha'_S = \alpha_S / \alpha_{evap} \tag{8}$$

$$\alpha_{evap} = \frac{p_i^{sat} \cdot \gamma_i}{p_j^{sat} \cdot \gamma_j} \tag{9}$$

$$\alpha'_D = \alpha_D \tag{10}$$

where α_{evap} is the vapor-liquid equilibrium selectivity which depends on the feed composition and temperature. For the toluene/iso-octane feeds used in this study, α_{evap} ranges from 0.771-0.586 at 100°C.

In this study, membrane performance is reported using the set of definitions given earlier in the text to be consistent with most of the literature on pervaporation. However, the

trends reported in this paper would be similar regardless of which framework is used. The above discussion shows the link between gas permeation and pervaporation membranes, and emphasizes the need for clear definition in terminology when discussing the two situations.

References

1. J.G. Wijmans, and R.W. Baker, A simple predictive treatment of the permeation process in pervaporation, J.Membrane Sci., 79(1993), 101-113

2. J.M. Smith, and H.C. Van Ness, Introduction to chemical engineering thermodynamics, 4th Ed., McGraw-Hill, New York, 1987

3. J. Gmehling, U. Onken, and W. Arit, Vapor-liquid equilibrium data collection, Vol I, part 6b, Dechema, Frankfurt, 1980

Appendix II Pervaporation apparatus and standard operating procedure

Pervaporation Apparatus

Pervaporation (PV) is a membrane technique for liquid separation. Liquid mixtures are fed to the upstream side of the membrane while the downstream side is a vapor state and typically is a vacuum. Some components in the mixture favored by the membrane material permeate through the membrane faster than the other components do. The driving force is the concentration gradient through the membrane thickness. As liquid molecules pass through the membrane, they evaporate and are eventually trapped by some cold source such as liquid nitrogen. The favored components are rich in the downstream vapor phase. Thus, the mixture is separated. A diagram of pervaporation system used our lab is shown in Figure A1. Figure A2, Figure A3 and Figure A4 are pictures of the pervaporation apparatus.

Standard Operating Procedure

Start

1. Connect collecting bottles to C1 and C2.

2. Close S1. Make sure that valve S4, S5 and S8 are closed, and S3, S2, S6 and S7 are open

3. Start the vacuum pump.

4. Assemble the permeation cell. Put it in the water bath. Fill it with liquid feed. Fill the liquid tank. Connect the cell to the permeation system.

5. Fill the water bath with water. Set temperature. Turn the heat on.

6. Immerse the cold trap in a dewar flask filled with liquid nitrogen. Open S8 slowly. Check the vacuum. When the vacuum is below 0.5 torr, open S4 and S5 slowly. Check the vacuum again. It should decrease below 1 torr and become stable.

7. When the water bath reaches the set temperature, start timing to condition the membrane. The conditioning time varies from 3 hours to 7 hours, depending on the permeation flux.

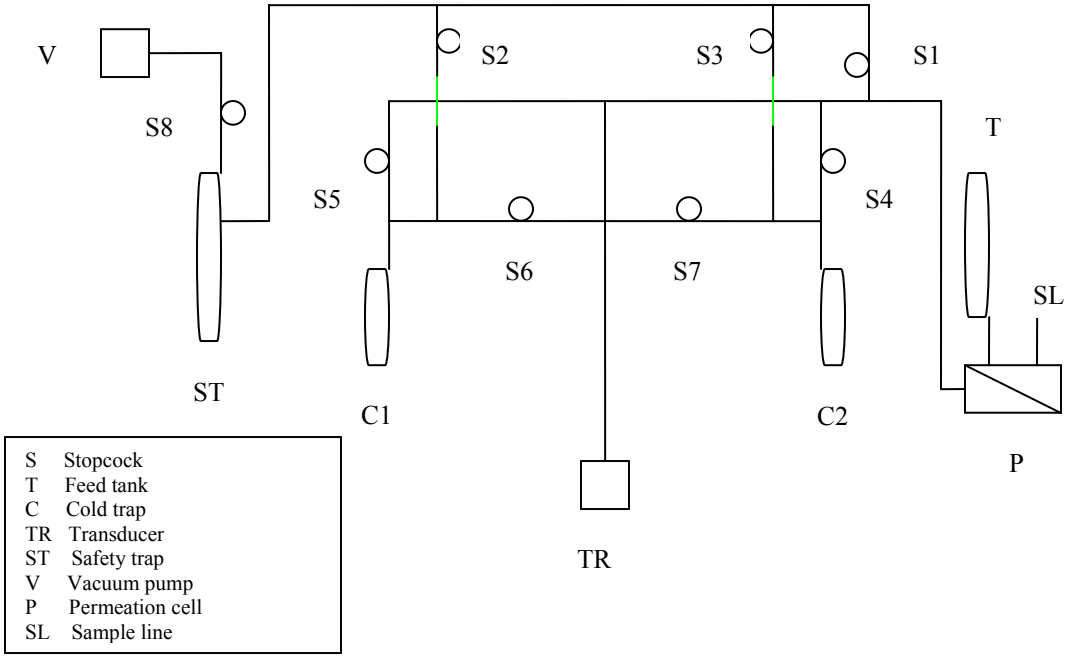


Figure A1 Diagram of a pervaporation system

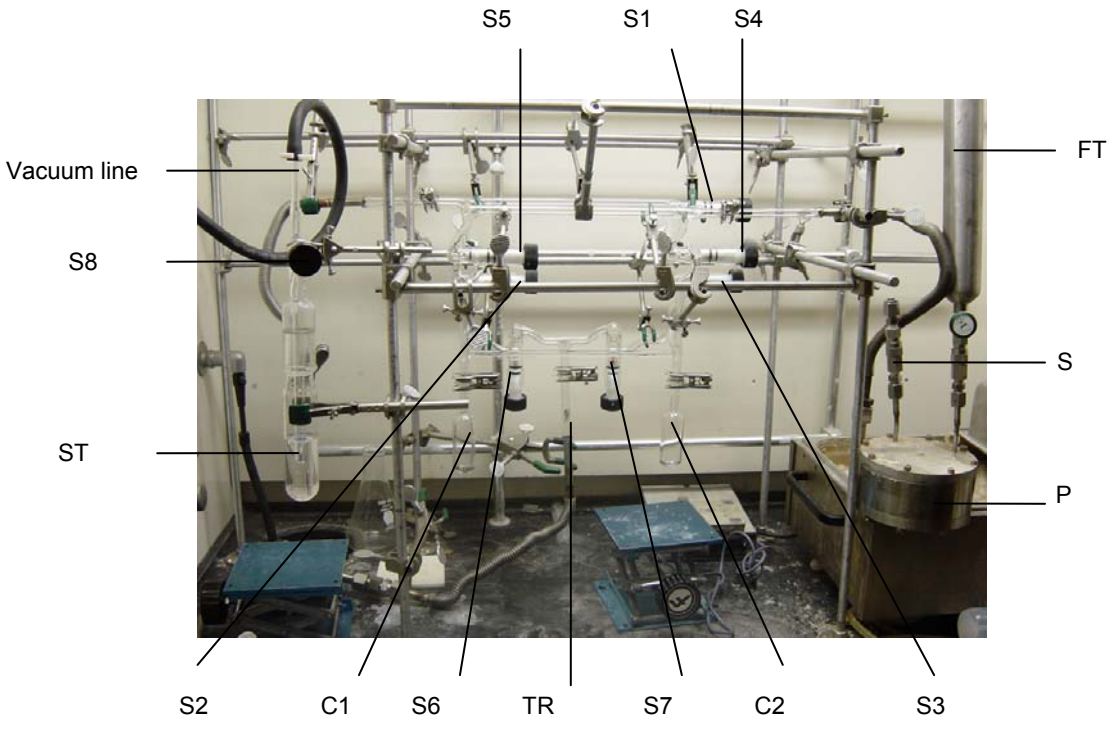


Figure A2 Picture of pervaporation apparatus used in our lab

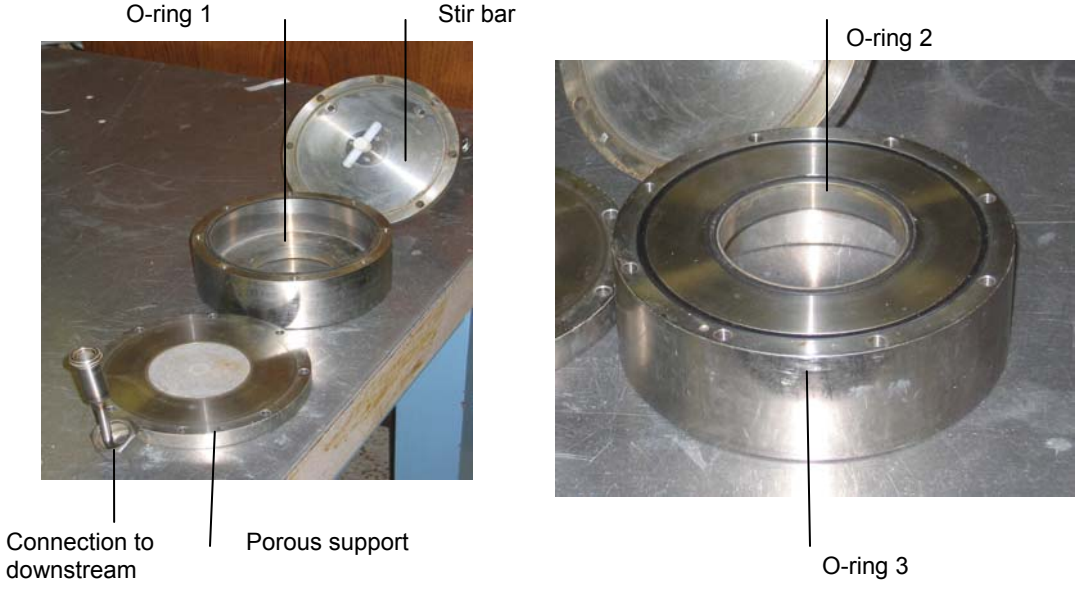


Figure A3 Picture of the pervaporation cell

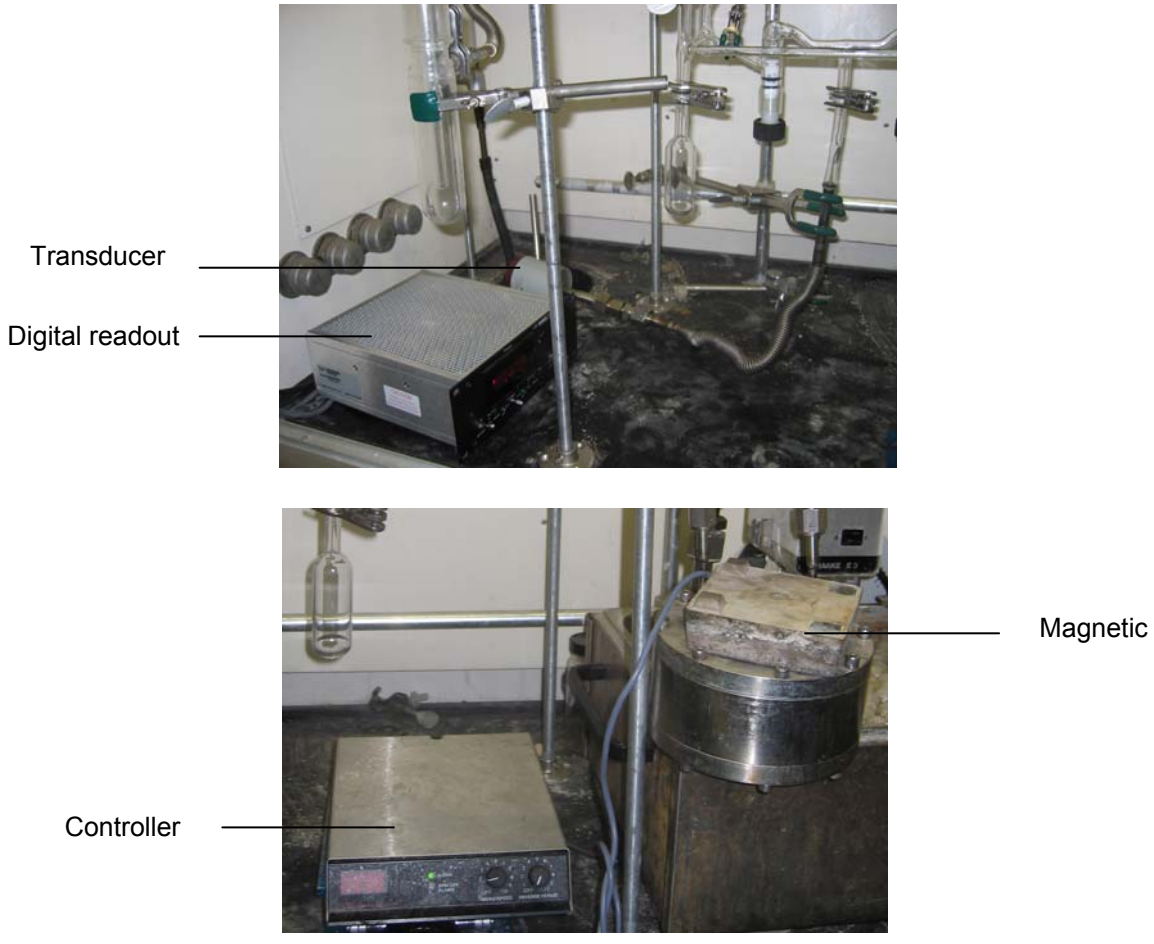


Figure A4 Pictures of transducer and magnetic

8. Refill water bath and cold trap dewar flask every hour. Check vacuum every 30 minutes.

9. When conditioning is done, close S3, S5 and S6. Immerse collecting bottle 1 in a dewar flask filled with liquid nitrogen. Close S2. When S2 is completely closed, start timing for sample collecting. At least 0.5 grams of sample are needed. The collecting time differs from 0.5 hour to 5 hours depending on the permeation flux.

10. Collect a feed sample from the sample line on the cell at the beginning of each permeation sample collecting. Collect another feed sample at the end of each permeation sample collecting.

11. Close S4. At the same time stop timing. Open S5 and S3. Close S7 then open S6. Take collecting bottle 1 off the system. Cover the bottle with a plastic top immediately. Let it warm to room temperature.

12. Start sample collecting at C2 with the step similar to step 9.

13. Weight the permeation sample. Transfer at least 0.2 grams of each sample (feed and permeation sample) to sample bottles. Analyze sample composition by GC or refractive index.

14. Calculate permeation flux and selectivity.

15. At least 2 permeation samples are needed. If their flux and selectivity do not agree with each other, collect more samples.

Finish

1. Turn the water bath heat off.

2. Drain the hot water in the water bath. Let the permeation cell cool down.

3. When the cell is cool, close S4 and S5. Take the cell off the system.

4. Transfer the liquid feed in the cell to the waste bottle and label it.

5. Close S8. Take the safety cold trap off and heat it. Transfer the liquid in it to the waste bottle. Clean and dry the cold trap. Connect it back to the PV system.

6. If necessary, disassemble the permeation cell and take the membrane out.

Emergency Stop

Carefully monitor the vacuum during a pervaporation run. If the vacuum pressure increases rapidly, close S8 and S4/S5. Stop water bath heating. Drain the water and wait for the cell to cool down. Take the cell off. Transfer the feed out of the cell. Check the membrane. In most cases, it is due to a membrane defect or over-swelling.

Notes

1. The PV system is made of glass. Handle carefully. Do not try to pull or twist any glass connection parts.
2. The water bath and the permeation cell are hot when the test is running. Be careful of hot surfaces and the steam from water bath.
3. Refill water bath and dewar flasks every hour. Keep water in the water bath and liquid nitrogen in the cold trap full when a test is in progress
4. Change vacuum pump oil every three months.

Appendix III Head-space GC method for toluene/iso-octane mixture sorption in 6FDA-DAM/DABA polyimide membranes

Total swelling

The equilibrium total swelling of toluene/iso-ocatne mixtures in the membrane was determined as follows. Precisely weighed dry membranes sheets (about 0.1 g each) were immersed into a toluene/iso-octane mixture at 100°C for 24 hours to reach equilibrium, then removed, wiped quickly with a Kim-Wipe and put into a weighing bottle. The transfer process takes less than 10 seconds. To correct for the evaporation of liquid during the transfer, the membrane weight was measured as a function of time using a microbalance, and then extrapolated to zero time to obtain the original weight of the wet membrane. The evaporation of the liquid during the transfer step was less than 2 wt% of the total amount of liquid in the membrane as shown in Figure B1.

Determine composition of toluene/iso-octane sorption

Equipment

1. HP 5890A gas chromatograph equipped with a SUPELCOWAX™10 Capillary Column with 30m x0.32 mm x 0.25 μm dimension.
2. a 5ml air-tight syringe and a 10μl micro-syringe
3. 20ml headspace vials with seals and Teflon silicone liners, sealer

GC operation condition

Oven temperature: 180°C

Initial temperature: 180°C

Initial time: 12 min

Final temperature: 220°C

Ramp speed: 20°C/min

Final time: 5 min

Injection temperature: 220°C

FID temperature: 250°C

Retention time for iso-octane: 10.2 min

Retention time for toluene: 10.7 min

Retention time for NMP: 13.7 min

Calibration curve

In an average case, the swelling of 6FDA-DAM/DABA membranes in toluene/iso-octane mixtures is about 20%. A membrane of 0.02g dry weight contains about 0.004g toluene and iso-octane after swelling. The composition of toluene/iso-octane in the swelling is between 60/40 wt% to 95/5 wt%.

1. Make 8 standard toluene/iso-octane liquid mixtures ranging from 60/40wt% to 95/5wt%
2. With a 10μl micro-syringe, inject about 0.004g (about 5μl) each of the standards into sealed vials containing 1ml NMP. Wait 12 hours at room temperature for vapor-liquid equilibrium.

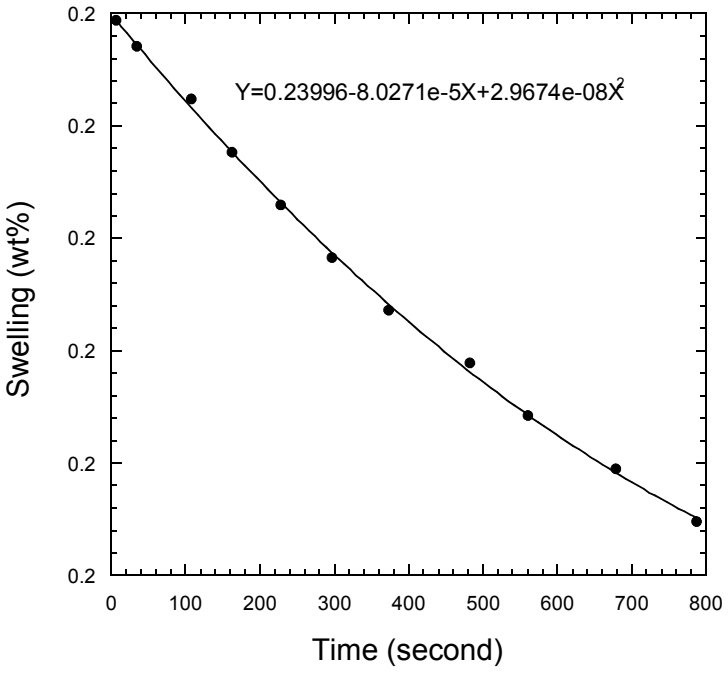


Figure B1 Total swelling of toluene/iso-octane in the membrane decays as the time membrane exposed in the air

Figure B2 Picture of air-tight syringe, headspace vial and sealer

3. Take 1ml vapor out of each vial with a 5 ml air-tight syringe and inject it into GC.
4. Calculate the peak area ratio of toluene versus iso-octane for each injection. Repeat step 3 and 4 twice for each sample. Average the peak area ratio.
5. Correlate the average peak area ratios with the toluene compositions of toluene/iso-octane standards and obtain an equilibrium curve.
6. Repeat step 2 by adding 1ml NMP, 0.02g 6FDA/BPDA (50%)-DAM dry film (Y') and 0.004g standard mixtures into vials.
7. Repeat step 3-6 and obtain the second equilibrium curve.
8. Repeat step 2 by adding 1ml NMP, 0.02g 6FDA-DAM/DABA (60%) dry film and 0.004g standard mixtures into vials.
9. Repeat step 3-6 and obtain the third equilibrium curve.

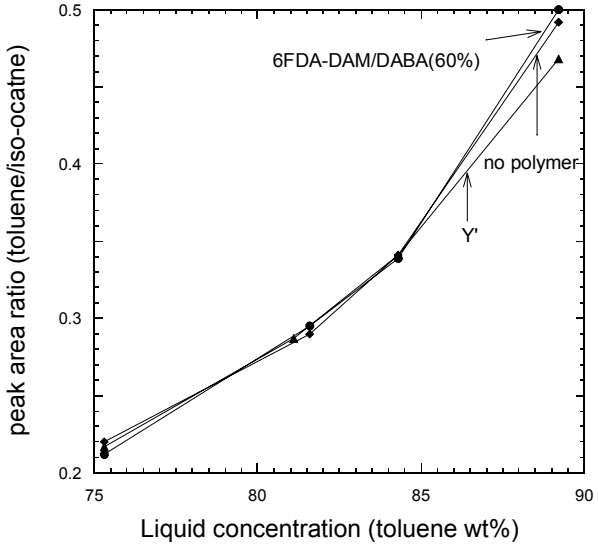


Figure B3 Three liquid-vapor equilibrium curves with different polymers in the systems.

Three equilibrium curves with different polymers in the equilibrium system are shown in Figure B3. The liquid-vapor equilibrium of the NMP- toluene/iso-ocatne system is almost identical to that of the NMP-toluene/isooctane-6FDA-DAM/DABA(60%) system. 6FDA/BPDA-DAM is a commercial polyimide with the chemical structure shown in Figure B4. The liquid-vapor equilibrium of the 6FDA/BPDA-DAM system is almost identical to that of the other two systems when toluene concentration in the liquid standards is below 85%. As the toluene concentration in the liquid standards increases, the equilibrium starts to show some difference. When the toluene concentration in the liquid standard is 89%, the equilibrium difference between the 6FDA/BPDA-DAM system and the 6FDA-DAM/DABA system is about 5%. The presence of different polyimides in the equilibrium systems does not affect the partition between the liquid and vapor phases. The equilibrium curve of the NMP-toluene/iso-octane system is used as the ultimate calibration curve for convenience. Figure B5 is a typical calibration curve for the liquid-vapor equilibrium of a toluene/iso-octane/NMP system.

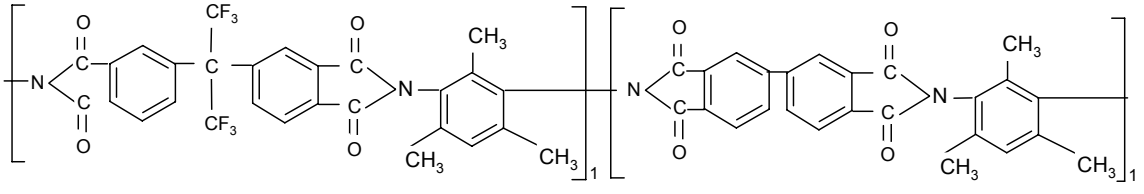


Figure B4 Chemical structure of 6FDA/BPDA-DAM(Y')

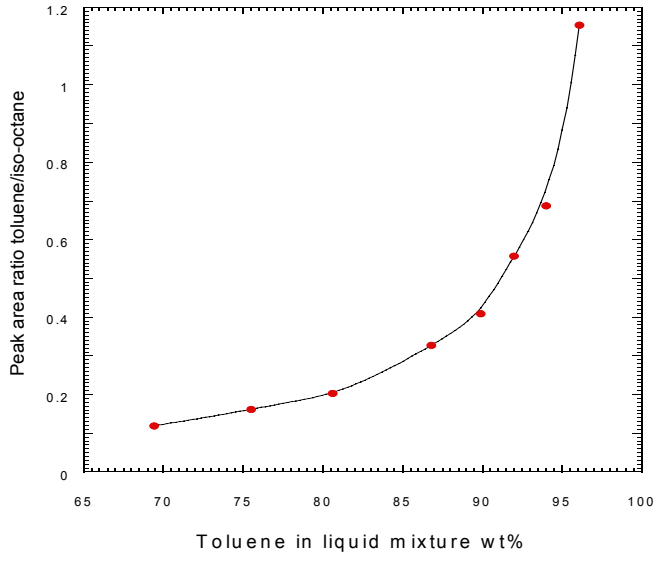


Figure B5 Calibration curve for the liquid-vapor equilibrium of toluene/iso-octane/NMP system.

The effect of toluene/iso-octane amount in the equilibrium system was also considered. Two samples were prepared; sample 1 with 1ml NMP and 0.004g toluene/iso-octane mixture (75/25%), sample 2 with 1ml NMP and 0.002g toluene/iso-octane mixture (75/25%). The peak area ratio difference between these two samples is less than 0.5%. In a certain range, the absolute amount of toluene/iso-octane in the system does not affect the equilibrium.

Sorption samples

A membrane sheet (dry weight about 0.02g) that had been equilibrated with a liquid toluene/iso-octane mixture at 100ºC was wiped and transferred into a vial containing 1 ml

NMP and dissolved. Repeat step 3 and step 4. Obtain the toluene/iso-octane composition swelled in the membrane from the calibration curve.

APPENDIX IV Masking of Carboxylic Acid in polyimides for GPC Tests

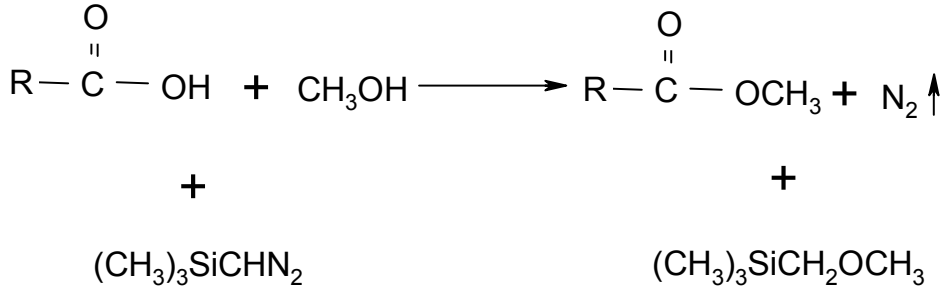
Most of the polyimides in this study contain carboxylic acid units, which is harmful to the GPC columns used to determine the polymer molecular weight. Therefore, all the polyimides in this study are treated with (trimethylsilyl) diazomethane to mask the carboxylic acid before the GPC tests. The chemical reaction involved is shown in Scheme C1.

Procedure

1. Dissolve about 0.005 grams of a polyimide material in a 25 ml flask with 10 ml THF and 5 ml methanol.

2. Add 0.5 ml (trimethylsilyl)diazomethane into the flask and wait for 30 min.

3. Vaporize the solvents and dry the polyimide in a vacuum at 60°C



Scheme C1 Reaction of (trimethylsilyl)diazomethane with carboxylic acid

Appendix V Refractive index for toluene/iso-octane liquid mixture composition

Concentration of toluene/iso-octane liquid mixtures is commonly analyzed by gas chromatography. In this study, A Fisher ABBE-3L refractometer was used to analyze the composition of liquid toluene/iso-octane mixtures because of its quickness and convenience. The pictures of the refractometer are shown in Figure D1 and Figure D2.

Procedure

1. Turn the power switch on, and wait at least 10 min to warm up the lamp.
2. Open the top prism case, and clean the top prism and the measurement prism with acetone. Dry the surfaces with Kim-Wipe.
3. Apply two drops of liquid sample on the measurement prism with a dropper. Close the top prism case immediately.
4. Adjust both the height and rotation of the illuminator for the best contract in the reflection borderline. Using the handwheel, set the borderline on the cross hair intersection, and achromatize it with the compensator dial.
5. Depress the contract switch and read the sample value in index of refraction.
6. Open the top prism case, and dry the measurement case with Kim-Wipe.

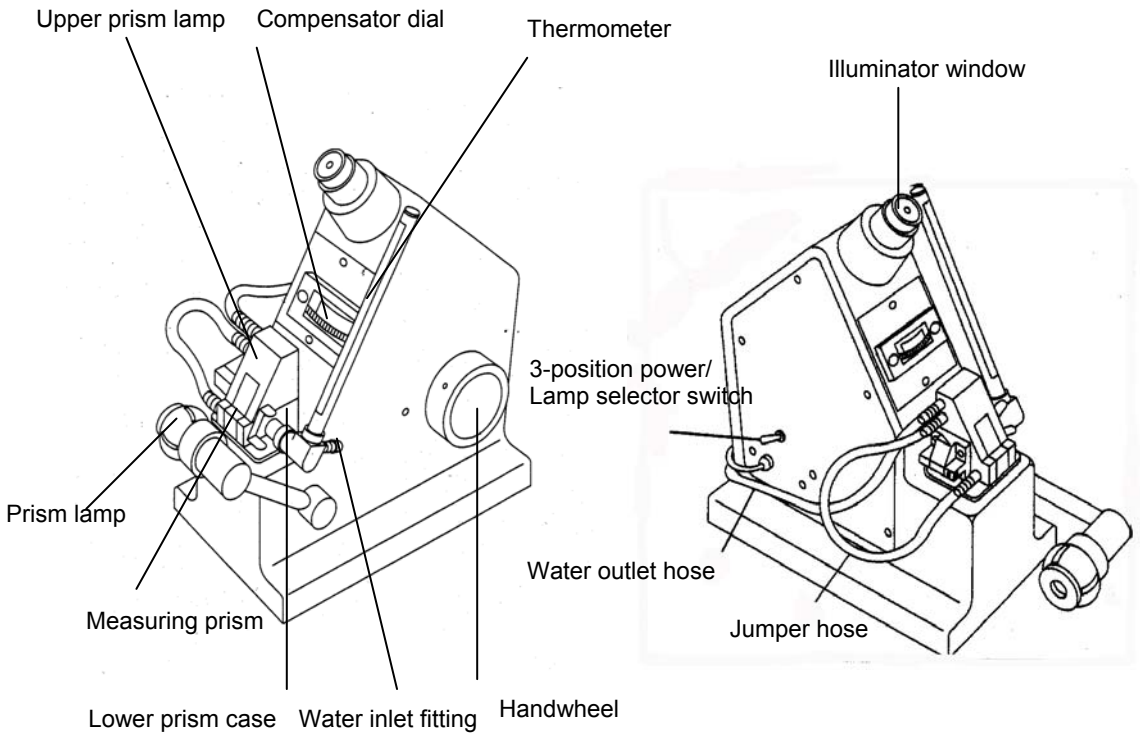


Figure D1 Pictures of Fisher refractometer

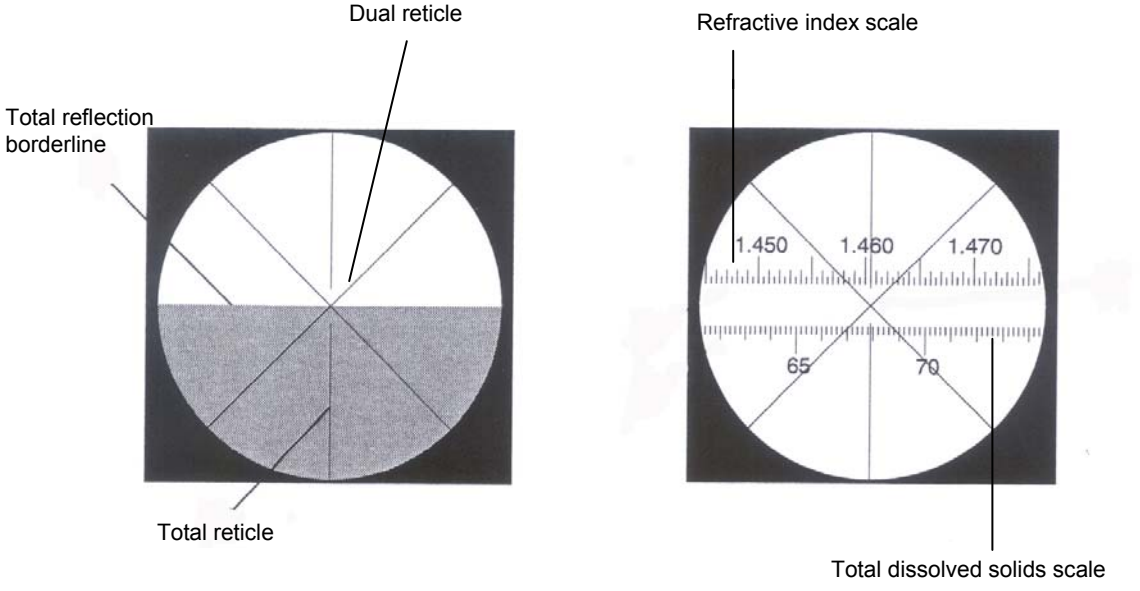


Figure D2 Pictures of illuminator

Calibration

Twenty standard samples are prepared with concentrations ranging from 30 wt% to 100 wt% toluene, and the refractive indices were measured. The calibration is plotted in Figure D3. The results from refractive index measurements are compared with those from gas chromatography measurement, and the difference is within 3%.

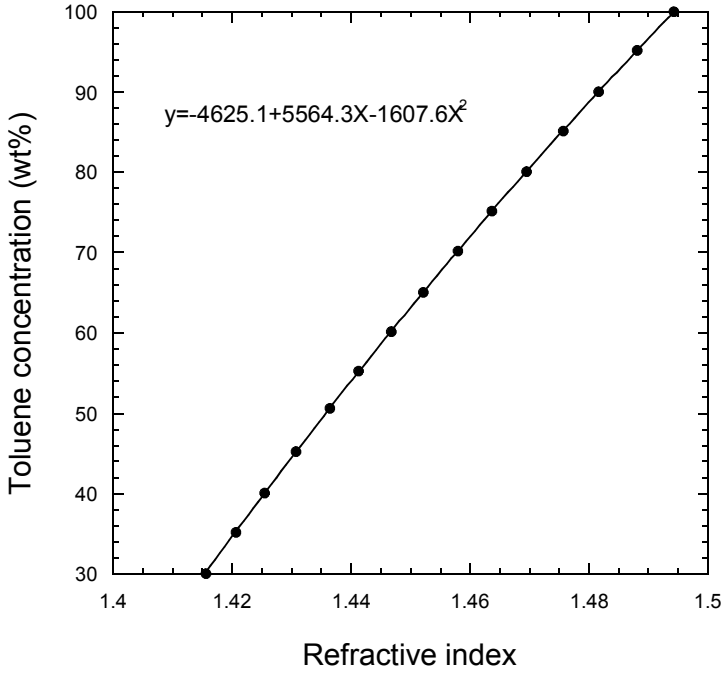


Figure D3 Refractive index calibration of toluene/iso-octane liquid mixtures

Appendix VI Effect of GPC calibrations on measured molecular weight

Gel Permeation Chromatography (GPC) has mainly three different calibration methods: conventional calibration, universal calibration and triple detection. Molecular weight and polydispersity of the polyimides used in this study were characterized by GPC with the conventional calibration. Samples were treated by (trimethylsilyl)diazomethane to mask the carboxylic acid groups in the polyimides before the tests to avoid any possible harm carboxylic acid unit may have to the GPC column. In conventional calibration molecular weight is solely determined by the relationship between the solution elution volume (retention time if a constant flow rate is used) and molecular weight of monodisperse polystyrene standards. Thus, the molecular weight obtained is relative to polystyrene. Triple detection is a new technique to obtain absolute molecular weight, using the information collected from light scattering detector and refractometer [1, 2].

A same polymer sample may have different molecular weight results obtained from conventional calibration and triple detection calibration due to the difference in calibration mechanism. To clarify the effect of calibration methods on polymer molecular weight, some of the polyimides used in this study were also measured by GPC with triple detection calibration. These samples were NOT treated by (trimethylsilyl)diazomethane before the tests. Besides the possible harm to the GPC column, the existence of carboxylic acid groups in the polyimides may change the chain size in solution because of the hydrogen bonding, and the retention time, consequently.

The change of retention time will definitely affect the molecular weight results from the conventional calibration, but not those from triple detection calibration. Table E1 show that the molecular weight measured by triple detection calibration is significantly higher than that measured by conventional calibration. The polydispersity measured by triple detection is significantly lower than that measured by conventional calibration.

Table E1 Molecular weight of 6FDA-DAM/DABA polyimides measured by triple detection GPC

	Conventional calibration		Triple detection calibration	
	Mn	Mw/Mn	Mn	Mw/Mn
0%DABA chemically imidized	26700	2.8	45000	1.4
0%DABA thermally imidized	23900	2.3	34624	1.5
10%DABA thermally imidized	31900	2.6	58240	1.2
10%DABA thermally imidized mono-ester	30200	2.8	46200	1.3

The molecular weight and polydispersity measured by conventional calibration and triple detection are not comparable because of the difference in calibration mechanism. Conventional calibration gives molecular weight relative to polystyrene, and triple detection measures the absolute molecular weight. Consistency in calibration is required in use of GPC to avoid any confusion caused by comparison of molecular weight measured by different calibrations.

References

1. GPC manual, http://www.tmi.utexas.edu/manual_gpc.pdf
2. Principles of triple detection GPC,

   http://www.viscotek.com/technotes.php4?menu=4&submenu=21

Appendix VII Calculation spreadsheets used in this study

Polyimide synthesis

Monomer Purification

Date 29-Apr-04

Name: Wenyuan Xu

Batch Size: (g) 2

MW Repeat Unit (g/mole): 595.1

Monomer	Mole Fraction	# mmole	Theoretical Charge Wt. (g)	Theoretical Reagent Volumes	Sublimation Yield Factor
6FDA	1.00	3.361	**1.4930**	TEA (mL)	
DDBT	0.00	0.000	**0.0000**	1.40	
DAM	0.67	2.240	**0.3366**	AcAn (mL)	
DABA	0.33	1.120	**0.1704**	0.95	N/A
6FpDA	0.00	0.000	**0.0000**		
			2.0000		

Raw Monomer				*Purified Monomer*	
Type	Mass g	Sublimation Temp ˚C	Heater Setting	Total Mass g	Actual Charge Wt. g
6FDA		(230˚C)	2.6		
BPDA		(290˚C)	3.5		
DAM		(80˚C)	5.0		
DABA		N/A	N/A		
6FpDA		(190˚C)			

Observations

NMP will be the solvent. Solids concentration will be ~ 15%.
11.3mL NMP needed.

Reactor Setup

Observations

100 mL round bottom flask with purge through septum.

Monomer Addition

Observations

Color: _____	Exotherm (Y/N): _____
Viscosity: _____	Gel Formation (Y/N): _____
NMP Added (mL): _____	Reaction Time (hr): _____

Polymerization

Action	Time	Δt (min)
Add TEA/AcAn		
Ramp to 100 ºC		
React at 100 ºC		

Purge Gas: House N2 **Purity:**	
Initial Pressure psig	Final Pressure psig

Observations

Waste Disposal

Component	Nominal Value mL	Actual Volume mL
Methanol	1000	
TEA	25	
AcAn	25	
NMP	30	
Molecular Sieves	60	
Filter Paper	1	

Waste Bottle Used

Mono-esterification

6FDA-DAM/DABA(33%) **Date** 22-Apr-04

Covalent Crosslinking **Name:** Xu

Batch Size: (g)	2.00	Solvent Volume (mL):	20.0	Solids Concentration
MW Repeat Unit (g/mole):	595.1	Solvent		9.1%

Monomer	Mole Fraction	# mmole	Theoretical Charge Wt. (g)	Crosslinking Agent	Diol Excess Factor	
6FDA	1.00	3.361	**1.4930**	ethylene Glycol	100	
BPDA	0.00	0.000	**0.0000**	g/mole		
DAM	0.67	2.240	**0.3366**	66.0	Time (hrs)	Temperature (^{o}C)
DABA	0.33	1.120	**0.1704**	Specific Gravity	18	140
6FpDA	0.00	0.000	**0.0000**	1.0140		
			2.0000			

	Acid Catalyst	
ethylene glycol	p-toluene sulfonic acid (g)	p-TSA/COOH
mL	0.0100	0.047
7.3		

Observations

Calculation of solubility parameter and fractional free volume

group	amount	E	V	ΣE	Solubility parameter of repeart unit
phenyl tri-sub	2	31940	33.4	180630	26.86899
phenyl penta-sub	0	31940	-4.6		
_CH3	0	4710	33.5		
_CF3	2	4270	57.5		
C	1	1470	-19.2		
_CO_	2	17370	10.8		
_N-_	0	4190	-9		
_COOH	2	27630	28.5		
_O_	0	3350	3.8		
_CH2_	0	4940	16.1		
Al	0	13810	-2		
NH-	2	8370	4.5		
phenyl bi-sub	0	31940	52.4		

For copolymers	E	V	ratio	solubility parameter of copolymer
6FDA-DAM	197820	283.7		26.65633
6FDA-DABA	211320	249.7		
BPDA-DAM	187810	187.9	0	
6FDA-6FpDA	225640	388.4	0	
6FDA	151750	187.8	1	
DAM	46070	95.9	0.9	
DABA	59570	61.9	0.1	
6FpDA	73890	200.6		
6FDA amic acid	180630	250.2	0	

Fraction Free Volume
Van der Wals volume

unit	Vc	amount	ΣVc
phenyl 1 sub	45.85		
phenyl 3 sub	40.8		
phenyl 5 sub	38.3		
CO	11.7		
N	4.3		
NH	4		
C	3.3		
CH3	13.67		
CF3	21.3		
COOH	19.7		

repeat unit	MW	Vc	ratio	film density	Vt	FFV
6FDA-DAM	558	259.7	0	1.33	419.5489	0.195302
BPDA-DAM	408	213.7	0			
6FDA-DABA	560	243.4	0			
BPDA-DABA	410	196.5				
6FDA-6FpDA	742	315.34	0			
6FDA-6FmDA	742	315.4				
6FDA amic acid	476	198.3	0			
6FDA	440	182.9	1			
DAM	118	76.8	1			
6FpDA	302	132.5				
DABA	120	60.5				

Polyimide	Density(g/cm3)	solubility parameter (Jcm-3)1/2
6FDA-DAM	1.338	26.4
6FDA-6FpDA	1.455	24.1
6FDA-6FmDA	1.475	24.1
6FDA-DAM/DABA(33%)	1.38	27.3
6FDA-DAM/DABA(60%)	1.414	28
6FDA-6FpDA/DABA(33%)	1.448	25.4
Y'	1.302	28.6
6FDA-DABA		29.8
6FDA-DAM/DABA(33%) with 4% amic acid	1.367	27.21
6FDA-DAM/DABA(33%) with 15% amic acid	1.38	27.08
6FDA-DAM/DABA(10%) chem	1.35	26.66
6FDA-DAM/DABA(10%) therm	1.339	26.66
6FDA-DAM chem.	1.338	26.4
6FDA-DAM therm	1.33	26.4

FFV	1/FFV
0.19	5.263158
0.202	4.950495
0.184	5.434783
0.183	5.464481
0.18	5.555556
0.196	5.102041
0.171	5.847953
0.191	5.235602

0.184	5.434783
0.189	5.291005
0.1952	5.122951
0.19	5.263158
0.1953	5.120328

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